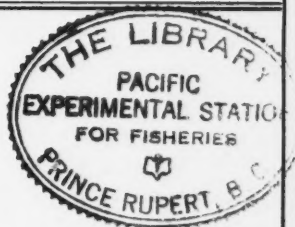


CANADIAN JOURNAL OF RESEARCH

VOLUME 16

JUNE, 1938

NUMBER 6



CONTENTS

SEC. A.—PHYSICAL SCIENCES

- The Variation of the Electrical Conductivity of the Atmosphere
with Height—*D. C. Rose* - - - - - 107

SEC. B.—CHEMICAL SCIENCES

- The Heats of Adsorption of Alkalis by Standard Cellulose
—*J. L. Morrison, W. Boyd Campbell, and O. Maass* - - - 195
- The Reaction of Oxygen Atoms with Methane—*E. W. R. Steacie*
and *N. A. D. Parlee* - - - - - 203
- The Polymerization of Isobutene—*E. W. R. Steacie and G. Shane* 210
- Contribution to the Study of Distyrenes—*Léo Marion* - - - 213

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows:

- A. Physical Sciences
- B. Chemical Sciences
- C. Botanical Sciences
- D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world, are as follows:

	<i>Annual</i>	<i>Single Copy</i>
A and B	\$ 2.50	\$ 0.25
C and D	2.50	0.25
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under the authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.



Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 16, SEC. A.

JUNE, 1938

NUMBER 6

THE VARIATION OF THE ELECTRICAL CONDUCTIVITY OF THE ATMOSPHERE WITH HEIGHT¹

By D. C. ROSE²

Abstract

The conductivity of the atmosphere has been measured during flights in aeroplanes near ground level and up to about 16,000 ft. Seven flights were made during the autumn and winter of 1936-1937. The Gerdien type of conductivity apparatus was used. An attempt was also made to measure potential gradients by the radioactive collector method. This method was impractical, probably because of charges acquired by the aeroplane. It did, however, serve to indicate the presence of intense local space charges such as charged clouds. On one flight, observations were taken near a thunderstorm, but owing to difficulties in interpretation no conclusions regarding the exact nature or location of the charges could be drawn. The conductivity increased rapidly with height in a manner in general agreement with the data of other observers. Positive and negative conductivities were found to be equal, within the experimental error, at heights between about 1000 and 10,000 ft. At higher altitudes the negative conductivity was greater than the positive. The presence of clouds and frontal discontinuities usually caused a reduction in continuities.

Introduction

While a great deal is known about the quantities describing the electrical state of the atmosphere at the surface of the earth, relatively few investigations have been carried out on the variation with height of such quantities as conductivity, space charge, potential gradient. A review of early experimental work on the subject covering the years from the first experiments of Franklin in 1750 until about 1928 has been prepared by Gish (1, pp. 182-186). Observations were taken with the aid of kites, balloons, and aeroplanes. In general, the conductivity has been found to increase with altitude fairly uniformly except for departures that may be due to haze layers or clouds. The potential gradient is generally believed to decrease with altitude, though observations do not always agree in the amount of decrease. The potential gradient is very difficult to measure, and no doubt varies considerably; consequently, no great agreement among individual observations should be expected. The ionic density is also thought to increase somewhat with altitude, though measurements are relatively few, and, owing to the existence of different kinds of ions, there is often uncertainty in regard to the actual property that is being measured.

¹ Manuscript received February 7, 1938.

Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada.

² Physicist, National Research Laboratories, Ottawa.

A valuable contribution to the knowledge of atmospheric electric phenomena was made in the flight of the stratosphere balloon "Explorer II" on November 11, 1935. The data obtained have been published by Gish and Sherman (2, pp. 94-116). Conductivity measurements were made at heights up to 72,000 ft., and, from these and comparison with cosmic ray data, deductions that were unexpected were made regarding the variation of mobility with height and the distribution of condensation nuclei.

The object of the present experiments was to investigate the possibilities of measuring atmospheric electric quantities during flights in aeroplanes, and to make further studies of their variation in different types of weather. It was also hoped that by taking observations near thunderstorms or cumulus clouds that might develop into thunderstorms, further information could be added to that already existing on the process of the building up of the electric charges that cause thunderstorms. Conductivity and potential gradient measurements were taken, and the results show that the potential gradient measurements are of little value, but the conductivity measurements were reasonably successful and in good agreement with previous work. Only once was it possible to observe effects near a thunderstorm.

The work is a continuation of work undertaken in 1931, in which conductivity observations were taken during four flights (4). In plotting the results of the 1931 flights the values for mobilities of positive and negative ions were assumed, and the results were plotted in terms of small ion density rather than of conductivity. As the values of the mobilities were very uncertain, and, as Gish and Sherman have pointed out, so little is known of the variation of mobility with height (2, p. 105), the method of expressing the results in the previous paper (4) is of little value. Therefore, the results of two of the early flights will be rediscussed here.

Conductivity Apparatus

Apparatus

The Gerdien type of conductivity apparatus was used. Fig. 1 is a schematic sketch of the tube, electrometer, and switch used to connect the electrometer to the conductivity apparatus or to the potential gradient apparatus. The design was somewhat different from that used in the 1931 flights, in that the

tube was larger and the potential was applied to the cylindrical tube surrounding the collecting electrode instead of to the electrode itself. This cylinder, to which the potential was applied, was supported in an outer shielding tube as shown. The important dimensions of the apparatus were: inside diameter of tube, 7.60 cm.; length of tube, 33 cm.; diameter of collecting rod, 0.79 cm.; length of rod, 31.25 cm.

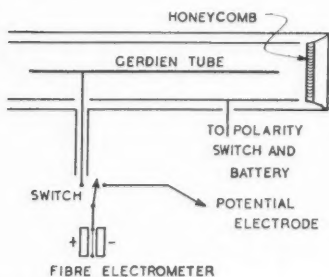


FIG. 1. Schematic diagram of apparatus.

The rod was supported on an amber insulator attached to the honeycomb at the entrance, and by a single insulated support that connected it to the electrometer at the other end. Amber insulation was used throughout. The conductivity was measured by observing the rate of movement of the electrometer fibre over a few divisions of the scale, and was given by

$$\frac{C_1 K \frac{dx}{dt}}{4\pi CV},$$

where C_1 is the capacity of the whole insulated system, collector and electrometer, and C is the capacity of the collector and its supports. K is the factor by means of which the electrometer deflection, X , is reduced to volts, and V is the voltage applied to the tube surrounding the collecting electrode. C_1 and C were measured by comparison with a standard variable condenser, and were found to be 71.9 $\mu\text{mf.}$ and 9.6 $\mu\text{mf.}$, respectively. The voltage applied to the tube was usually 229 volts, and, since the voltage of the collector was never allowed to change by more than a few volts from ground, the above differential expression, rather than its integrated form, was used to calculate conductivities.

A honeycomb about $\frac{3}{4}$ in. deep with $\frac{1}{8}$ in. square holes and kept at ground potential was placed at the entrance of the tube. The insulating ring between the flared entrance and the high potential cylinder was so fitted that there were no irregularities in the surface and no flow of air between the inner and outer tubes. The necessity for the honeycomb is discussed in the paper (4) describing the 1931 flights. It is shown that the air in the tube would be very turbulent if this honeycomb were not used. Since the velocity of the air through the honeycomb is very high, the number of ions lost to its metal surfaces by diffusion would be negligible. Hence the loss in conductivity due to its presence would be limited to the loss of ions brought into contact with the metal by the motion of the air through it. As only a small part of the total air passing through the honeycomb can come into contact with the metal, the loss due to its presence would not be expected to be appreciable. A reversing switch in the battery circuit made it possible to change the potential of the cylinder quickly from positive to negative.

The conditions under which this equipment will measure conductivity are also discussed in the previous paper (4). The velocity of the air in the tube, and the potential, dimensions, and other factors must be such that a radius r_0 given by the equation

$$r_0^2 \approx \frac{2MVL}{v \log \frac{b}{a}} \quad (1)$$

must be less than the radius of the inner tube b ; V is the potential, M the mobility, L the length of the tube, v the velocity of the air stream, and a the radius of the collecting electrode. An air speed indicator was carried on one of the flights, and at various times during the flight the pilot tube was held in the rear end of the conductivity tube in order to obtain an approximate

measure of the air speed. The speed indicated under observation conditions was about 90 miles per hr. If the worst case at high altitudes be taken, with a mobility of say 3 cm. per sec. per volt per cm. and an air speed in the tube of 3000 cm. per sec. (about 67 m.p.h.), then the value of r_0 given by Equation (1) is 2.5. This is sufficiently less than the radius of the tube (3.8 cm.) to ensure that a condition of saturation would not be reached.

In the 1931 flights the conductivity tube was mounted on the bottom of the plane a few inches below the fuselage, the apparatus being supported through the camera hole. In the present apparatus the tube was mounted about a foot under one wing; the supports projected out through a window and held the tube 8 or 10 in. from the cabin fuselage. A high wing, cabin monoplane was used. Owing to the fact that the velocity of the ions is small compared with the speed of the aeroplane, any fields produced by charges on the aeroplane would have no effect on the conductivity. The possibility of ionization due to the propeller motion, heat from the engine, or contamination by exhaust gases must also be considered. It is doubtful whether temperatures high enough to cause any appreciable ionization would be encountered, and, in view of the relative speed of rotation of the propeller and its forward motion through the air, it is doubtful whether enough air would be ionized to affect the conductivity seriously. The exhaust manifold carried the gases well below and to the rear of the conductivity tube; hence, apart from the possibility of leaks in the manifold, no contamination would be expected. As the probability of there being a leak small enough to affect the results without changing the order of magnitude of the conductivities was small, no special tests for such contamination were made. A location for the conductivity tube well clear of the slip stream would have been preferable, but practical considerations made it impossible to mount it sufficiently far from the cabin to be completely out of the stream of air that passed close to the engine or propeller.

The Potential Gradient Apparatus

An attempt was made to measure the potential gradient near the plane by means of radioactive collector. The radioactive material (radium DEF mixture) was located in a small shielded, but well ventilated, chamber on the end of a rod placed in the air stream. This rod was used in two positions. In Flights 1 to 4 it extended vertically through the bottom of the cabin so that the radioactive head was about level with the bottom of the wheels during flight; it was about 2 ft. below the fuselage. It was therefore necessary to draw it up during take-off and landing. In Flights 5 to 7 the rod was placed through a side window and supported by a strut pointing downwards at an angle of about 45 degrees. The end extended about 2 ft. beyond the wing struts, and was about $1\frac{1}{2}$ ft. off the ground, when the aeroplane was on land, and 6 ft. out from the bottom edge of the cabin fuselage. The same electrometer was used for measuring the potential gradient and the conductivity. Its suitability for both purposes will be discussed in the next paragraph. That this method did not prove successful as a measure of

potential gradient was not entirely unexpected. Its failure is due to charges acquired by the aircraft or perhaps by the rod supporting the collector as it moves rapidly through the air. It did, however, prove useful in one flight near a thunderstorm, when sudden changes in potential could be observed readily.

The Electrometer

The electrometer employed in the 1931 flights was reconditioned and used in the present experiments. A single Wollaston wire fibre about one inch long, suspended between two knife edges, was used. The knife edges were charged to plus and minus 45 volts. The electrometer and galvanometer used in conjunction with resistance thermometers for relative humidity measurements were mounted on a vibration proof support. With some alterations in design, after the first flight, a very satisfactory method of support was achieved.

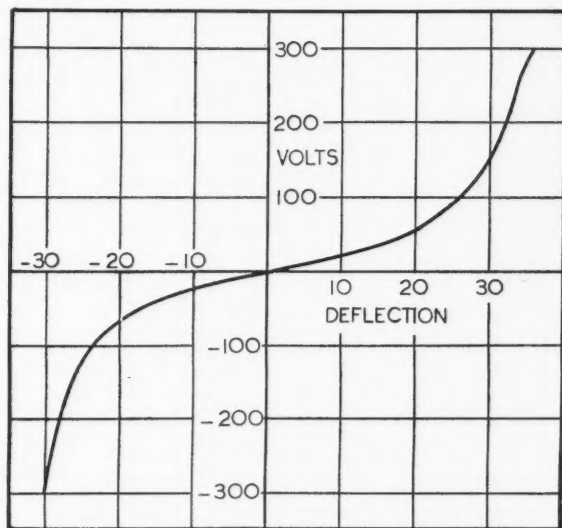


FIG. 2. Typical calibration curve for the electrometer.

The electrometer was particularly well adapted for the purpose, in view of the shape of its calibration curve. Fig. 2 shows a typical calibration curve. At low voltages the sensitivity was of the order of one division per volt and reasonably linear over a range of ± 10 volts. The conductivity measurements were always taken over a range of less than 10 divisions on each side of the zero positions. As the voltage was increased, the sensitivity decreased to such an extent that voltages as high as about 350 could be read as accurately as the conditions of the experiment required.

The electrometer did not retain its calibration as steadily as might have been desired. The sensitivity changed somewhat with temperature, particularly at the higher voltages. Calibration curves were prepared before and after each flight, and some points could be determined during flight. By comparing these points with the calibration curves, a curve could be obtained which was within 5% of the correct value over the range in which conductivities were measured. For conductivity measurements, the slowest rate of movement of the fibre measured was of the order of a division in two minutes. Rates up to several divisions per minute were observed as the conductivity increased at high altitudes. It is estimated that the probable error would be less than 10% for high altitudes but perhaps somewhat higher in the low conductivities at low altitudes, allowance being made for a slight zero shift with different altitudes of the plane.

Meteorological Instruments

In addition to conductivity and potential gradient, relative humidity, temperature, and pressure were measured. For relative humidity measurements, two resistance thermometers were used, one of which was wet periodically throughout the flight. These were connected to a bridge circuit (3) which gave a measure of the difference between wet and dry bulb temperatures. These thermometers were placed in the slip stream. By an alteration in the circuit one of them could be used to measure the dry bulb temperature. Since the thermometers were under one wing and well shielded from direct sunlight and well ventilated, no special radiation shields were provided. The temperature was also measured by a strut thermometer placed well out of the slip stream. The temperature in the slip stream was usually about two degrees higher than that of the surrounding air, owing to the fact that the air cooling the engine was mixed in the slip stream. Relative humidities were calculated by means of the partial water vapor pressure in the slip stream and the temperature of the surrounding air as measured by the strut thermometer. Smithsonian meteorological tables were used for the reductions.

A Tycos aneroid barometer was also carried. This was of a meteorological, aeroplane type, and had been calibrated against standards before the series of flights. Approximate altitudes were noted by observing the altimeter on the plane's instrument panel.

Experimental Procedure

The procedure adopted in each flight was as follows: After the apparatus had been mounted in the aeroplane and notes taken on the weather conditions on the ground, the flight was started. The first observations were usually taken at an altitude of 1000 ft., as read on the aircraft altimeter. After that, observations were taken at 2500 ft., 4000 ft., and at levels every 2000 ft. higher. Conductivity readings were taken while the aeroplane was flying level and as nearly as possible at constant speed. Usually four conductivity observations were taken at one level, two of each sign. The temperature readings were taken between conductivity observations; this ensured that the

plane had been flying at a constant level long enough for the thermometers to reach equilibrium. After the conductivity and temperature readings were recorded, a reading was taken of the potential indicated by the radioactive collector. The pressure also was noted, usually several times, at each level. During ascent between levels, potential gradient readings were taken, and water was sprayed on the linen covering of the wet thermometer.

Clouds were avoided as much as possible during ascent, but during descent, if clouds were within reach, conductivity and potential measurements were taken while the aeroplane was flying just over the top of the clouds. Potential measurements were made during the descent through the clouds, and another set of conductivity and potential measurements were taken just below the clouds. No consistent observations other than these were made on conductivity during descent. To avoid turning while readings were taken and during climbs, the plane was usually flown more or less in a straight line, usually starting from Ottawa towards Montreal, and returning over the same route, or perhaps turning southward and flying along the St. Lawrence river for a short distance before returning to Ottawa. The country covered is a relatively flat area between the Ottawa and St. Lawrence rivers, and, though the course varied, the flights usually covered a distance of from 50 to 100 miles east or southeast of Ottawa and return by a triangular route. The time required to complete the flight was about three hours. In Flights 1 to 3, owing to imperfect engine adjustment for high altitude, only 10,000 to 11,000 ft. was reached, but in Flights 4 to 7, 15,000 to 16,000 ft. was reached, this being about the ceiling for the plane used, unless unreasonably long times were taken to climb between levels.

As the planes used for these flights were also used for other purposes which took precedence over the atmospheric electric observations, and because the author had other work on hand, the flights had to be arranged at times convenient to the parties concerned rather than at the times of occurrence of chosen weather conditions.

Results

Variation of Conductivity with Altitude

The results of each flight will be discussed separately and then all results will be summarized, particular reference to the observations near clouds being left for a later section. The recent flights are numbered one to seven in the order in which they were made, and the two 1931 flights, which are rediscussed, are numbered 3A and 4A; these were Flights 3 and 4 mentioned in the previous paper.

Flight 1—September 1, 1936. Fig. 3

At the beginning of the flight the sky was mostly overcast with stratus clouds a few hundred feet thick and at a height of about 5000 ft. Towards the end of the flight the sky cleared slightly. Weather maps show a weak front passing over Ottawa on September 1. At 8 hours there was a centre of low pressure over the Gulf of St. Lawrence; a high, north of Hudson Bay;

and another low, west of Lake Michigan. This was the only flight during which the aeroplane flew through clouds on ascent. Fig. 3 shows the positive and negative conductivity, relative humidity, temperature, specific humidity, and partial potential temperature. The meteorological observations show a different air mass above about 6000 ft., or above the cloud level. The conductivity, instead of increasing continuously, shows a discontinuity at the cloud level and an excess of positive conductivity above the cloud. The potential gradient observations indicated that the cloud probably contained a considerable quantity of electric charge. However, as will be discussed

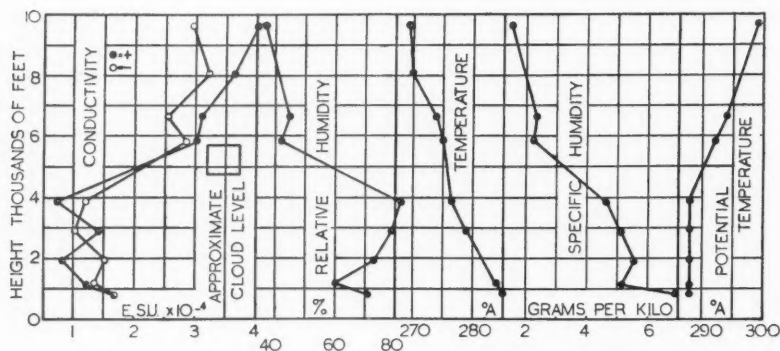


FIG. 3. Flight I.

later, just what the potential gradient apparatus measured was not very certain; consequently, conclusions drawn from observations with it are somewhat speculative. As the air above the cloud layer was very stable (probably polar continental), it is unlikely that the excess of positive conductivity was due to a flow of ions or condensation nuclei from lower levels into this region. A possible explanation lies in the reduction of the negative ion density owing to a tendency to neutralize positive charge in the upper part of the cloud. This is also indicated by the fact that the negative conductivity is considerably below the average of that observed in all flights at the levels from 6000 to 10,000 ft., while the positive conductivity is about equal to the average (see Fig. 12).

During the summer of 1936, including the time at which Flights 1 to 4 were made, potential gradient observations were taken on the ground at a country station about seven miles northwest of Ottawa (5). The results showed a definite relation between the passage of fronts and disturbances in the potential gradient.

On September 1 a minor disturbance in the potential gradient that started shortly before noon was noted. As there was no precipitation, this was probably due to increased turbulence in the lower air. The conductivity record below cloud levels also showed virtually no increase of plus or minus

conductivity up to cloud levels, probably owing to an unusual distribution of condensation nuclei due to the turbulence near the frontal surface.

Flight 2—September 11, 1936. Fig. 4

The sky was completely overcast, there being two definite cloud layers. The lower layer consisted of very irregular cumulus or stratocumulus clouds of varying heights lying between 2000 to 6000 ft. and covering about 40 to 60% of the sky. A small local thunderstorm occurred during the latter part of the flight, and observations were taken near it. These will be described later. The upper layer of clouds (altostratus) was well above the

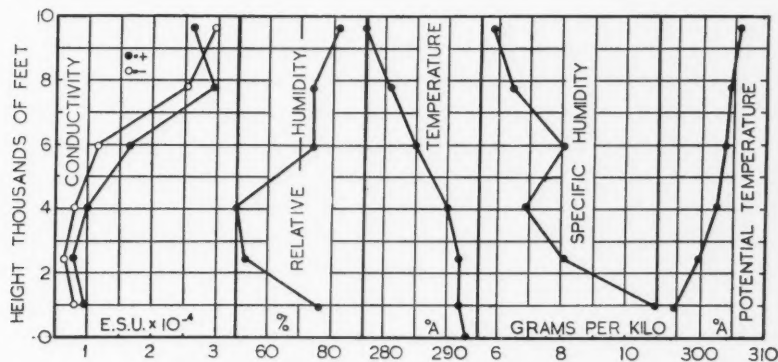


FIG. 4. *Flight 2.*

highest level reached, probably at about 20,000 ft., and the sky was completely overcast. The weather maps and barograph record show a system of two or more weak fronts moving across the continent from the west. The conductivity measurements showed values much less than average up to 6000 ft., about the upper limit of the lower cloud level. Then a rapid increase was noted at an altitude of 7800 ft. and no definite further increase at the highest level at which observations were made, 9620 ft. The positive conductivity was higher than the negative except at the highest level.

Flight 3—September 22, 1936. Fig. 5

On September 22, as on September 11, two cloud layers were noted. The lower layer consisted of a few scattered fractocumulus clouds at about 4000 to 6000 ft. The upper layer almost covered the sky and was quite thin and very high, probably altostratus. The weather conditions are shown in detail in Fig. 7 of the paper (5) describing the potential gradient observations on the ground. The 8 a.m. weather map for September 22 shows a weak cold front in an east-westerly direction just north of Ottawa. On September 23 this had become a warm front and had receded some distance farther north. At the time of flight, while the aeroplane was flying at an altitude of 6100 ft., the temperature suddenly rose about 2° C. The point is marked "X", in

Fig. 5. The specific humidity curve shows a discontinuity at this point. Apparently the aeroplane had entered a different air mass. The conductivity curves are abnormal. Very low values were noted at 1000 and 2800 ft., then after the usual increase up to about 6000 ft., abnormally low values were again noted at the higher altitudes. No doubt these abnormal values were the result of changes in the ionic equilibrium near the frontal surface, though there were no clouds near the line of flight.

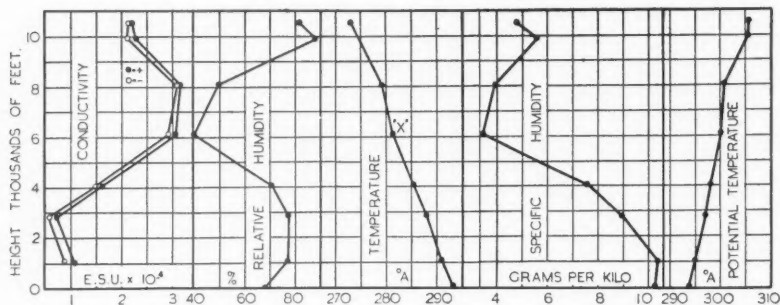


FIG. 5. Flight 3.

Flight 4—October 9, 1936. Fig. 6

At the beginning of this flight no clouds were visible, but when an altitude of a few thousand feet was reached a small bank of stratocumulus was noted some distance to the east, and a few scattered fractocumulus some distance to the south. A detailed description of the weather conditions is given in Fig. 8 of the report (5) on potential gradient observations on the ground. The weather map showed an anticyclonic condition with a depression west of Lake Superior. The barometer was falling slightly at the time of the flight; the centre of the anticyclone had therefore just passed. There was considerable haze and a light northeast wind typical of conditions just after the passing of a centre of high pressure. The conductivity shows a fairly steady increase with height up to the highest level reached, the values of the positive and negative conductivities being virtually the same.

Flight 5—November 16, 1936. Fig. 7

The sky was almost covered with low broken stratocumulus or nimbo-cumulus clouds, and occasional light snow flurries were noted. The weather map shows a deep depression over the Labrador coast, a high over the Mississippi Valley, and another high over northwestern Hudson Bay. The barometer was rising rapidly owing to the anticyclone spreading over the southeastern United States. The low broken clouds, the shape of the potential temperature curve, and the fact that the air was quite bumpy at low levels indicate considerable turbulence at levels up to 5000 or 6000 ft. Above this level the air was quite clear and very cold, the temperature dropping to

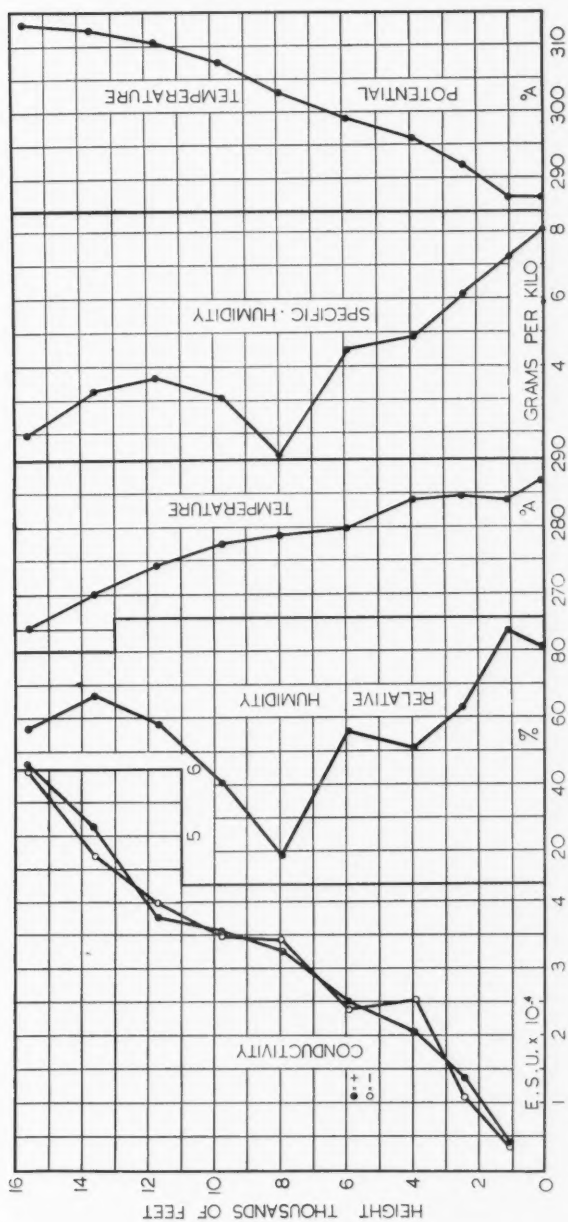


FIG. 6. Flight 4.

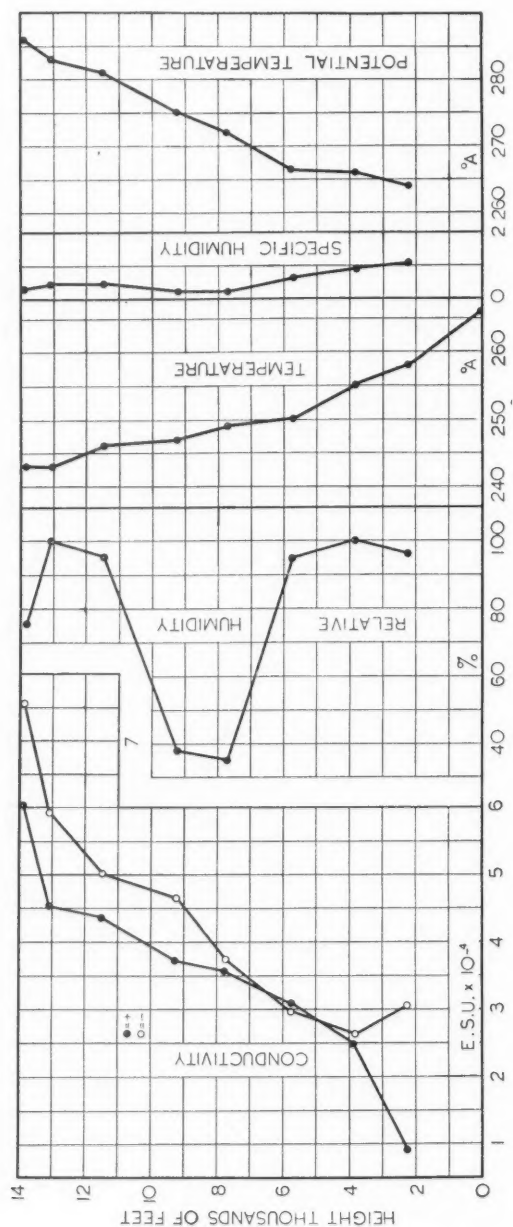


FIG. 7. Flight 5.

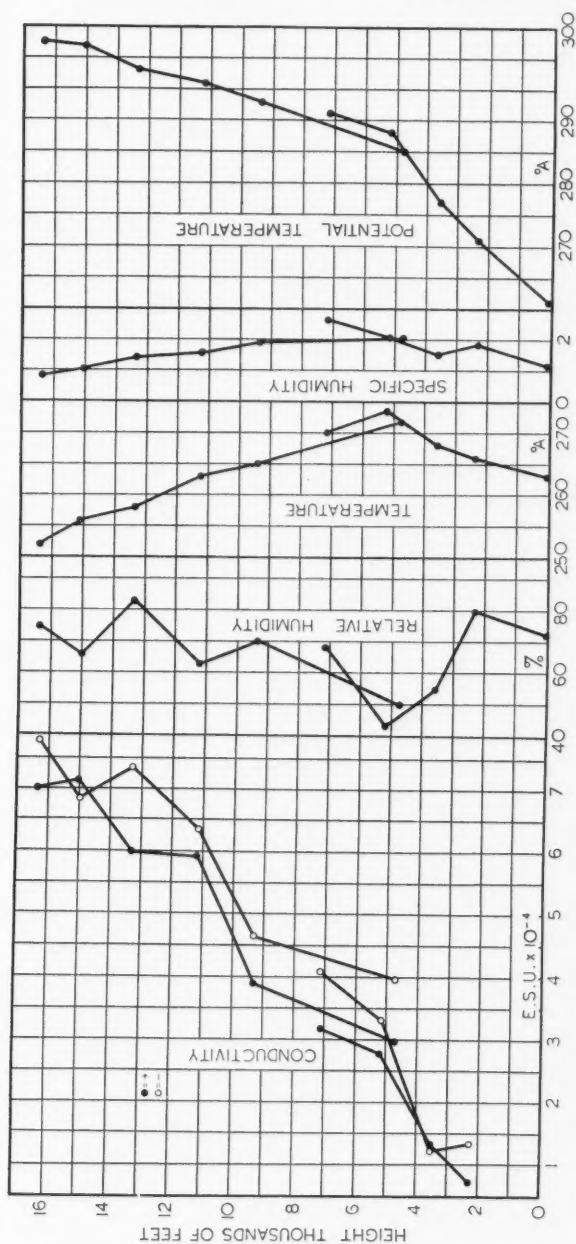


FIG. 8. Flight 6.

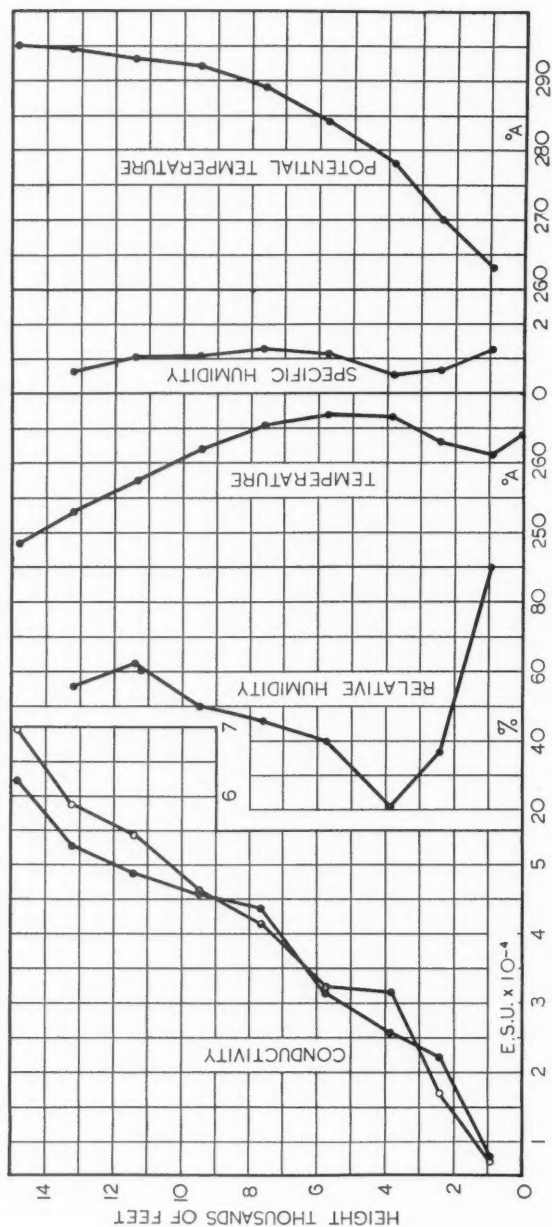


FIG. 9. Flight 7.

-30° C. at 13,000 ft. The conductivity increased fairly consistently with height, with the exception that an unusually high negative value was noted at the lowest point observed. No definite reason for the high negative conductivity at this point is apparent, though the cloud formation was such that local space charges might be expected and an unusually high potential gradient was recorded at the same level. Unfortunately the continuous recording of potential gradient at the ground station outside Ottawa had to be discontinued about November 1; the general behavior of the potential gradient at the time of this and subsequent flights was therefore not observed. The negative conductivity was considerably higher than the positive at levels of 9000 ft. and higher. It should be noted, however, that owing to the very low temperatures encountered in this flight, the calibration of the electrometer was not known as accurately as it was in other flights.

Flight 6—December 9, 1936. Fig. 8

On the morning of December 9 the sky was clear, but at the time of the flight it was completely overcast, there being two definite layers. The lower layer, uniform stratus, covered about half the sky with a definite boundary, and was about 3000 ft. high. The upper layer, thin altostratus, was well above the highest point reached. The 8 a.m. weather map shows a centre of high pressure over the Gulf of St. Lawrence, and a series of lows over the middle western parts of the United States and the prairie provinces in Canada. The barometer was falling as a centre of low pressure was obviously approaching from the west. After the plane had reached a height of about 7000 ft. it was brought to the ground to permit a passenger to disembark, and the flight was then resumed. The curves in Fig. 8 are broken accordingly. The agreement in values found at overlapping levels is reasonably good. During ascent the observations at 3600 ft. were taken near the edge of the lower cloud bank, but no attempt was made to fly in the cloud. Throughout most of the flight the negative conductivity was higher than the positive.

Flight 7—February 16, 1937. Fig. 9

The weather on February 16 was typical of an approaching anticyclone. The barometer was rising, the visibility very good, and the sky clear, except for scattered cirrus clouds forming cirrostratus. A light northwest wind was blowing. The weather map shows an elongated centre of high pressure running northward from the upper Great Lakes. Two fairly deep lows are shown on the Atlantic coast; one north of Newfoundland and one centered over the eastern United States just north of Florida.

The conductivity increased steadily with altitude, positive and negative values being nearly the same at low altitudes, and negative values being higher at heights above 10,000 ft. The conditions of this flight probably represent as nearly as possible those to be expected in fresh polar continental air coming over completely snow-covered and mostly uninhabited territory. It is interesting to note that the conductivity curves more closely resemble the average

of those for the seven flights (Fig. 12) than does any other, though the conductivity is higher at low altitudes.

Flight 3A—April 18, 1931. Fig. 10

Flight 4A—June 7, 1931. Fig. 11

Conductivity of one sign only was measured during ascent and of the other sign during descent in all the 1931 flights. Hence Figs. 10 and 11 show the meteorological observations during both ascent and descent. In Flight 3A there was but little difference in conditions, but in Flight 4A the humidity curves for ascent and descent are rather different. The relative humidity observations, however, for descent are not very reliable at points where the temperature was below freezing, because the water supply was usually frozen after two or

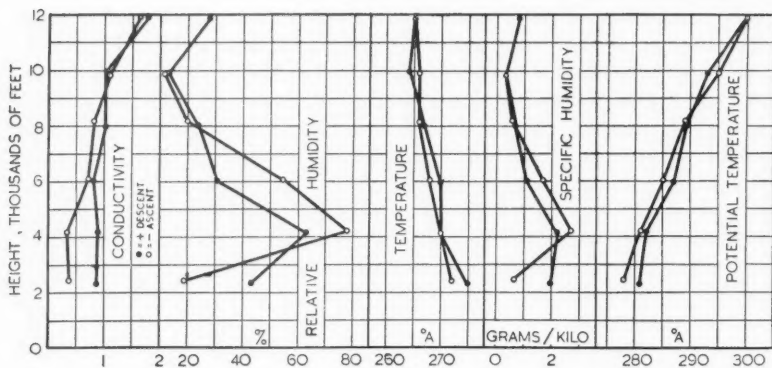


FIG. 10. *Flight 3A.*

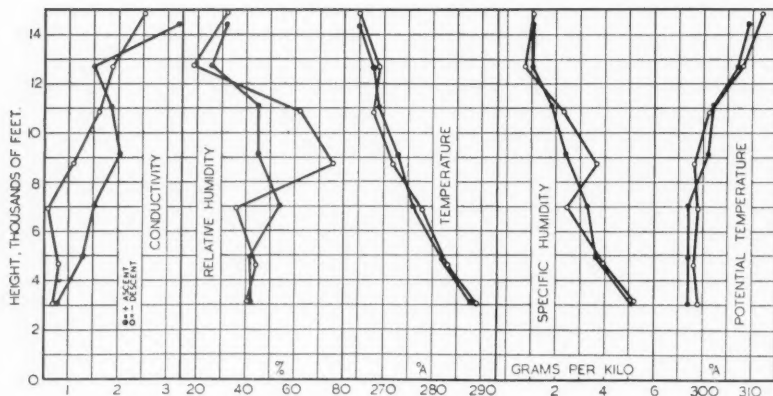


FIG. 11. *Flight 4A.*

three hours' flying, and the wick could not be properly wetted between observations. In the present work (Flights 1 to 7) precautions were taken to keep the water supply from freezing; and, also, the thermometers were in a more accessible position for wetting.

Weather notes on the days of Flights 3A and 4A are not as complete as were those of the recent flights, though as the 1931 flights were all taken in reasonably fine weather, the weather was anticyclonical and the sky was clear or only few fractocumulus clouds were present. As the reduction factor, necessary to reduce to conductivity the readings taken with the 1931 apparatus was not very accurately known, the conductivity units in Figs. 10 and 11 are arbitrary. In general, however, the conductivity increases with height, though the amount of the increase seems considerably less than that in the seven recent flights.

Mean Variation in Conductivity

The mean curves for the variation of positive and negative conductivities with height, as shown in Fig. 12, were obtained in the following way. As the conductivities on different flights were not all measured at exactly the same altitudes, those at a height from, say, 500 to 1750 ft., were averaged and the heights were averaged, and thus a mean value was obtained.

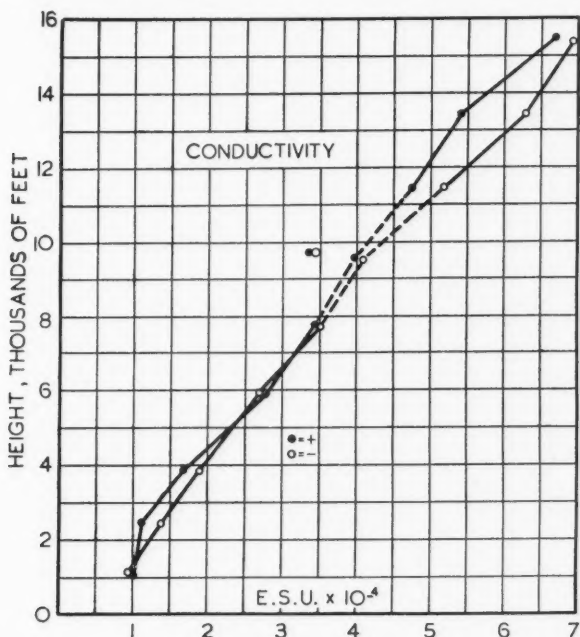


FIG. 12. Mean conductivity curves.

A second point included observations at heights between 1750 and 3250 ft., another between 3250 and 5000 ft., another between 5000 to 7000 ft., and so on. As most of observations were taken at or near 1000, 2500, 4000, 6000 ft. etc., the averages represented closely the means of the conductivities taken at these levels. The data obtained in the 1931 flights are not included in the average. If all observations were included, the portion of the curves shown by the broken lines would include the points to the left of that part of the curve at conductivities of $+3.3$ and -3.4 , and at a height of 9705 ft. instead of as shown. The points through which the curve was drawn at this level were obtained by excluding the observations at the highest altitudes on Flights 2 and 3, where there is an abnormal reduction in conductivity. In Flight 2 there was definite evidence of intense charges in nearby clouds; a thunderstorm was passed not very far from where the measurements were taken. In Flight 3, a frontal surface was encountered at an altitude of about 6000 ft. Certain points taken during Flight 1 might also have been excluded, as a front was encountered in that flight also. Their exclusion, however, would not have made very much difference in the shape of the mean curve.

Observations at ground levels have shown that on the average the potential gradient is positive, and a positive space charge is found. It is generally accepted that this falls off very rapidly with height; consequently, at the lowest point included in Fig. 12 no appreciable space charge would be expected. Once the space charge becomes negligibly small, the ratio of plus and minus conductivities must be equal to the ratio of the effective mobilities of the positive and negative ions present. In regions at low altitudes, in which the number of condensation nuclei is appreciable, the conductivity is reduced considerably by the presence of the nuclei, and it would be impossible to predict with any accuracy much about the ratio of positive to negative conductivities. Over a considerable range of much higher altitudes, in the stratosphere, where the density of nuclei is thought to be negligible, Gish and Sherman (2, pp. 94-116) found the ratio of the conductivities to be equal to that of the mobilities of positive and negative ions. In the present results (Fig. 12) the mean values of the positive and negative conductivities are almost equal at the lowest altitude. From about 1500 to about 5000 ft. the positive conductivity is slightly less than the negative, though in view of the small amount of data available, it is doubtful whether the difference is significant. Hence, from about 1000 to 10,000 ft. the curve indicates that the positive and negative conductivities are very nearly equal in magnitude. If one accepts the assumption that there is no space charge, then, in view of the fact that small negative ions are invariably found to have greater mobilities than small positive ions, equal conductivities would indicate that the loss of small negative ions, due to combination with condensation nuclei or with large positive ions, is greater than the corresponding loss of small positive ions. Scrase (6) has estimated the combination coefficient of the various types of ions, and finds that the combination coefficients of small negative ions with uncharged nuclei and

with large positive ions are greater than the corresponding coefficients for small positive ions with uncharged nuclei or with large negative ions. Though he expressed some doubt as to the validity of the equations used, the results here are at least in qualitative agreement with the relative values of the coefficients found.

At the higher levels, above 10,000 ft., the effect of nuclei becomes less and the value of the negative conductivity becomes greater than the positive. The ratio (mean of three highest points gives 0.92), however, is higher than the value (0.78) found by Gish and Sherman (2, pp. 94-116) at still higher levels on the stratosphere flight. The transition to a nuclear free state would not be expected to take place rapidly, and would probably not be complete until the stratosphere was reached; a close agreement in this ratio is therefore not to be expected. The actual magnitude of the conductivities at different heights agrees reasonably well with the values found by Gish and Sherman and with those of Wigand (9, 10).

In regard to the differences in the curves in Figs. 3 to 11, there is little further to be said. Where obvious explanations of differences between individual curves and the mean curves exist, these are noted in the individual discussions of the flights. It should be noted that these curves represent conductivity observed on ascent only, where clouds were avoided as much as possible, and the aeroplane flew through no clouds except in Flight 1.

Potential Gradient Observations

That the method used for measuring potential gradient is impracticable when applied to observations taken in aeroplanes is shown by the following. First, the position of the potential electrode in the bottom of the plane was such that, in the normal earth's field, that is, positive with height, if the aeroplane and the collector electrode took up the potentials of the air at their corresponding levels, the potential of the collector electrode should be negative with respect to the plane. In fact, virtually all readings taken while the aeroplane was flying level and the sky was free from clouds were positive. Second, the nature of the readings when the plane was climbing, flying level, and descending was such that some effect other than the atmospheric electric field must have been predominant in the potentials measured, except when high potentials were encountered near charged clouds.

That the potential measurements are not reliable can be seen when the measurements of Flight 3 are examined. At the lowest altitude, 1080 ft., a steady potential of +35 volts* was observed while the aeroplane was flying level. As soon as the plane was put in a climbing attitude and the engine throttle opened accordingly, the potential started to decrease, dropping to values as low as -10 volts. While the aeroplane was flying level at the next altitude at which conductivity measurements were taken, namely 2830 ft.,

* It is difficult to estimate the gradient in volts per metre that this would represent, unless a model of the aircraft was constructed.

the potential rose to +143 volts. During the next climb between levels it dropped again to 45 volts, and when the flying was level at 4050 ft. it rose to +177 volts. This drop in potential occurred more or less consistently during periods of climb at low altitudes. Once altitudes of 8000 or 10,000 ft. were reached, the drop would be only a few volts, and on a few occasions an increase in potential during ascent was noted. During descent, with the engine idling, irregular variations in potential would sometimes take place, and sometimes it would merely decrease regularly until levels near ground were reached.

In view of these observations, the results of the potential gradient measurements are not considered worth publishing in detail, and only those taken when the aeroplane was flying near a thunderstorm will be shown. It was not entirely unexpected that this method of measuring potential gradient would not be satisfactory, because of the highly ionized state of the engine exhaust gases. Wigand (8) has shown that these may bear a net charge, and therefore the plane will have an opposite charge. Further, the potential observations are nothing more than a measure of the potential between an insulated rod and the plane. The action of the radioactive collector and the rod supporting it in a very rapidly moving air stream is uncertain. As the plane is constantly acquiring a charge owing to the effect of the exhaust gases, or by other means, and the electrode is constantly losing a charge owing to removal by the field of more ions of one sign than of the other, it is the difference between these two effects that will be observed. Apparently these effects under normal cloud-free conditions are such that the earth's field is reversed, and, from the magnitude of the voltages measured, the spurious effects appear to be greater than the normal earth's field.

Observations Near Clouds

During flight through clouds, conditions were changing too rapidly to permit conductivity readings to be made. Only readings on the potential gradient electrode were taken. The aeroplane flew through clouds during descent on Flights 2, 3 and 5, and a cloud layer was penetrated during ascent on Flight 1. On the other flights, either no clouds were present or they could not be reached easily.

The positive potential measured in normal, cloud-free areas, though it varied considerably in no consistent manner, was usually between about 50 and 200 volts. During flight near or through clouds, if potentials no greater than about 200 volts were encountered, the results were considered to indicate that no great local charges were present. If the potential measuring apparatus indicated voltages of several hundred volts, it was considered a fair indication that local space charges existed nearby. As the potential electrode was on the bottom of the plane, positive potentials would normally be expected to indicate a negative field. This might be due to a large negative charge higher up, a positive charge below, or a combination of both. Reversals in the field might mean that the aeroplane was flying through a centre of space

charge, or that a point was passed at which there was a field reversal due to, say, a combination of nearby local volumes of positive and negative space charges. Such a reversal usually occurs at ground levels when a thunderstorm passes overhead. However, during flight through clouds in which there is considerable space charge due to charged water drops, the potential difference between the plane and the collector will more likely be fixed by the relative amounts of charge picked up and lost by both, as the result of the water drops wetting the surface and then being blown off as a fine spray. The resulting potential would give a measure, not of the potential gradient, but of other effects. The fine spray blown off the struts and other parts of the plane can easily be seen during flight through rain or heavy mist. If the temperature is at or below the freezing point, and the cloud particles consist wholly or partly of ice crystals, the resulting charges acquired by the plane and collector would again be expected to be different. Hence, though charges were observed in clouds on three flights, the details of which are described below, unfortunately no conclusions as to their exact polarity or location can be drawn until better methods of observation are obtained.

In Flight 1, while the aeroplane was ascending it was necessary to fly through a fairly uniform layer of stratus clouds. During ascent towards the clouds the potential rose rapidly to about 400 volts at an altitude a little higher than 4000 ft., then as the aeroplane passed through the cloud the potential reversed to a high negative value (about -250 volts). Just above the cloud while the aeroplane was flying level at 6000 ft. it remained negative (-65 volts), then at higher levels became positive again. How much of the negative potential observed was due to the change in attitude of the plane, as described in the previous section, and how much was due to space charges in the cloud is uncertain. However, just below the cloud an unusually high positive potential was observed, and just above, a negative value was recorded when the aeroplane was flying level. It might be noted that the conductivity observations are not inconsistent with the assumption of a positive charge in the cloud.

In Flight 2, during descent, a small thunderstorm was passed, the line of flight lying a mile or two to the north of the centre of the storm. It was not known until after landing that the storm had developed into a thunderstorm, as no lightning was seen during the flight. The potential measurements taken as the plane flew towards the storm, at an altitude about equal to that of the top of the clouds, and then as the plane descended through the clouds around the outer edge of the storm centre, are shown in Fig. 13. The storm was quite small, and the cumulus cloud at its centre extended only up to about 7000 ft. The largest cloud shown in the figure represents the storm centre, and, if the path of the aeroplane as shown is considered to be in a vertical plane, the direction of flight being west, the storm centre was estimated to be about two or three miles to the south. Though considerable rain and mist was encountered, the only part of the flight which penetrated clouds of sufficient density to limit visibility to such an extent that ground or cloud forms

were completely obscured is indicated by *CC* in Fig. 13. The horizontal axis represents very roughly the distance in miles. The sizes of the clouds as shown should not be considered in relation to this scale, as the cloud areas could be drawn only roughly from memory after the flight and the few notes taken on cloud formation. The line of flight was sufficiently far away from the storm centre that no great turbulence was noted.

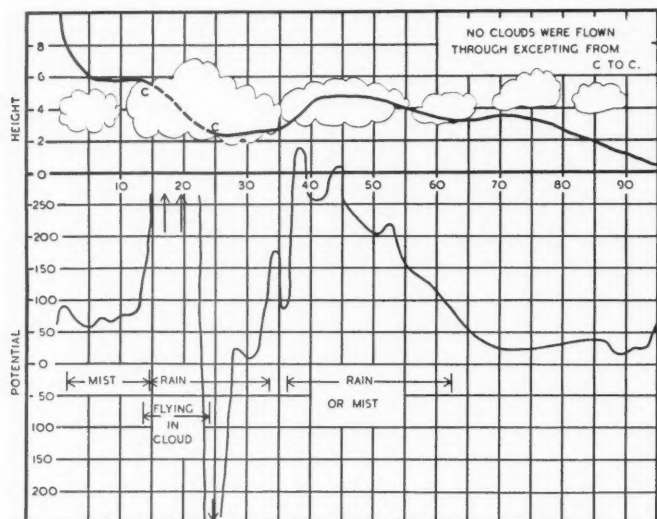


FIG. 13. Changes in potential during flight near a thunderstorm.

If it could be assumed that the potential electrode was behaving in the normal way, and that the electric charges involved were in the cloud at the storm centre, then the polarity of the cloud would appear to be opposite to that found in the Wilson type of thunderstorm. If it is assumed that the potential of the collecting electrode is fixed by the effect of water drops striking it, then the polarity it will assume for a given type of space charge is still ambiguous. A few conductivity measurements were taken shortly before the cloud was entered. Conductivities from 5 to 45 E.S.U. were noted but they were changing too rapidly to permit a decision to be made as to whether positive or negative was higher.

The only other occasion on which excessive potentials were noted was during ascent in Flight 5. During flight at the lowest level observed, namely, 2270 ft., an unusually high potential (about 400 volts) was recorded. At the same level the negative conductivity was much greater than the positive (see Fig. 7). This level was considerably below the base of the clouds, and, though no precipitation was noted when the observations were made, there had been a slight snow flurry just before the take-off, and another during the landing. Under such circumstances local space charges would not be unexpected.

On Flights 3 and 5 the aeroplane flew through clouds during descent. Small isolated clouds of the fractocumulus or fractostratus type were chosen. No changes of sufficient magnitude were noted in the potential measurements to indicate any quantity of local space charge.

To investigate the effect of clouds on conductivity on some occasions during descent, conductivity measurements were taken during flight just above the tops of clouds, and another set immediately afterwards just below the clouds. In Table I these are compared with the mean values of conductivities as shown by the curve in Fig. 12. Most of the differences are negative; that is, the presence of the clouds appeared to reduce the conductivity. Exceptions are shown in Flights 1 and 5. In both cases there is some evidence of local space charge in the cloud, and in Flight 5 the differences are small. The two sets of observations recorded during Flight 3 were taken some distance apart, and there was considerable difference in cloud level.

In conclusion it may be stated that the use of aeroplanes in studying atmospheric electricity could give a great deal of information about atmospheric electric effects if extended to regular flights and flights under chosen conditions. Some other method of measuring potential gradients should be

TABLE I

Flight and sign	Conductivities		Differences* from mean		Altitude, ft.	
	Above clouds	Below clouds	Above clouds	Below clouds	Above clouds	Below clouds
1 +	3.02	0.73	+0.32	-0.92	5860	3870
	2.85	1.22	+0.20	-0.63		
3 +	1.55	0.73	-0.7	-0.8	4890	3520
	1.35	0.88	-1.0	-0.9		
3 -	1.73	1.36	-1.2	-0.7	6290	4700
	1.54	1.13	-1.3	-1.1		
5 +	3.00	2.01	-0.2	+0.35	7260	3850
	3.12	2.21	-0.08	+0.3		

* Positive differences indicate conductivities higher than the mean value.

developed. A generating voltmeter would possibly be satisfactory, or a doublet might be used which would give a measure of the difference in potential between similar electrodes above and below the plane.

At present it is generally accepted that the process of building up charges to produce thunderstorms involves the forming and the breaking up of water drops, or their motion in ionized air (11). In Flight 2, in which there was evidence of charged clouds, considerable precipitation was noted in regions where high potentials were encountered. In Flight 1 no precipitation was observed, and in Flight 5, though no precipitation was noted at the point at which the high potential gradient was recorded, local snow flurries were

noticed shortly before and after the flight. The physical state of the cloud must be important. During Flight 5 the temperature at cloud levels was well below the freezing point; the cloud, therefore, probably consisted of ice crystals. If further measurements were made with improved apparatus, and more detailed attention were given to the nature of the clouds, it should be possible to obtain strong evidence for or against present theories regarding the generation of electric charges in thunderstorms.

Acknowledgments

The author wishes to thank the Department of National Defence for giving the flying time required for these experiments, and to thank the officers who did the flying. Meteorological information and advice given by Messrs J. Patterson and A. Thomson of the Meteorological Service of Canada was also greatly appreciated.

References

1. GISH, O. H. Actual and potential results from electrical exploration of the atmosphere. Trans. Am. Geophys. Union, Seventeenth Annual Meeting. 1936.
2. GISH, O. H. and SHERMAN, K. L. Stratosphere Series No. 2, National Geographic Society. 1936.
3. ROSE, D. C. Can. J. Research, 5 : 156-161. 1931.
4. ROSE, D. C. Can. J. Research, 5 : 625-635. 1931.
5. ROSE, D. C. Can. J. Research, A, 15 : 119-148. 1937.
6. SCRASE, F. J. The charged and uncharged nuclei in the atmosphere and their part in atmospheric ionization. Air Ministry, Geophysical Memoirs, 64. 1935.
7. SIMPSON, SIR GEORGE and SCRASE, F. J. Proc. Roy. Soc. London, 161 : 309-352. 1937.
8. WIGAND, A. Ann. Physik, 85 : 333-361. 1928.
9. WIGAND, A. Phys. Z. 22 : 36-46. 1921.
10. WIGAND, A. Ann. Physik, 66 : 81-109. 1921.
11. WILSON, C. T. R. J. Franklin Inst. 208 : 1-12. 1929.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 16, SEC. B.

JUNE, 1938

NUMBER 6

THE HEATS OF ADSORPTION OF ALKALIS BY STANDARD CELLULOSE¹

BY J. L. MORRISON², W. BOYD CAMPBELL³, AND O. MAASS⁴

Abstract

The heats of adsorption of aqueous sodium, potassium, and lithium hydroxides, and some salt solutions by cotton cellulose have been measured. The adsorption of alkali by cellulose seems to be ionic rather than molecular; more particularly, it appears to be closely related to the availability of the H^+ ion from the very weakly acidic cellulose, and of the OH^- ion from the electrolyte.

The nature of the adsorption of alkalis by cellulose has been the subject of considerable speculation. Fresh interest in this subject has been revived by a paper by Bancroft and Calkin (2), in which the authors report the results of measurements of a so-called true adsorption of sodium hydroxide on cellulose.

Generally two distinct methods have been used to measure the amount of adsorption, a change-in-titre method (9, 11, 15, 16, 17), and a centrifuge method (2, 6, 12). The results obtained by investigators using different methods, or even the same method, vary widely. As a consequence, different investigators are at variance regarding the theoretical deductions as to the adsorption mechanism concerned. Heuser and Bartunek (9) imply a molecular compound formation between the alkali and the cellulose molecules in proportions such as $(C_6H_{10}O_5)_2LiOH$, $(C_6H_{10}O_5)_2NaOH$. On the other hand, Bancroft and Calkin are of the opinion that a simple "adsorption" takes place. Neale (14), from considerations of measurements of heats of adsorption, postulates the formation of a hydrolyzable sodium cellulosate.

It was thought that further and more accurate measurements of the heats of adsorption of alkalis by cellulose might yield additional information in regard to the adsorption mechanisms involved. So far the only measurements of this type recorded in the literature are those of Barratt and Lewis (3), Neale (14), and Chilikin (5), who used sodium hydroxide. The present investigation includes the study of the adsorption by standard cellulose of sodium hydroxide, as well as of lithium and potassium hydroxides, and some salt solutions.

¹ Original manuscript received December 11, 1937.

Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada. This investigation was carried out in co-operation with the Forest Products Laboratories of Canada, Montreal, and formed part of the research program of that institution.

² Research Fellow, Canadian Pulp and Paper Association, Forest Products Laboratories of Canada, Montreal.

³ Consulting Physical Chemist, Forest Products Laboratories of Canada.

⁴ Macdonald Professor of Physical Chemistry, McGill University.

Experimental Technique

A description of the apparatus (a rotating adiabatic calorimeter) and the procedure has been given in a previous paper (13). All samples were taken from one lot of cellulose. The alkali solutions were made up to the desired strength and analyzed before being transferred by means of a weight pipette to the calorimeter, care being taken to prevent access of carbon dioxide. The sodium and lithium hydroxides were free from carbonate. The potassium hydroxide contained 2% of potassium carbonate. Measurements were also made with potassium carbonate, sodium chloride, and sodium-chloride-sodium-hydroxide solutions. All chemicals employed were of c.p. quality.

Results

The heats of adsorption of solutions of lithium, sodium, and potassium hydroxides, by standard cellulose, were determined. The data are presented in Table I and are plotted in Figs. 1 and 3. The best obtainable specific heat data (4, 8) were used to calculate the results, and the corrections for heat of vaporization were made from vapor pressure data (10, pp. 370 and 373).

The heats of adsorption of a sodium chloride and two potassium carbonate solutions by the standard cellulose were measured. A similar determination was made with a sodium-chloride-sodium-hydroxide solution prepared from the above-mentioned sodium chloride solution to which was added sodium hydroxide to the extent of 2.81% of the total solution. The values obtained for these miscellaneous determinations are given in Table II.

TABLE I
HEATS OF ADSORPTION OF ALKALIS BY STANDARD CELLULOSE AT 25° C.

Alkali	Concentration, weight %	Individual determinations, calories per gram dry cellulose				Mean, cal. per gm.
LiOH	2.66		12.38		12.50	12.44
	5.48		14.30		14.22	14.26
NaOH	0.95	11.49	11.17	11.18	11.47	11.30
	1.89	11.84	11.86	11.74	11.79	11.81
	4.28		12.55	12.55	12.66	12.58
	5.40			13.24	13.29	13.27
	6.55		13.60	13.54	13.69	13.61
	8.20		14.78	14.84	14.53	14.71
	11.39			17.85	17.73	17.79
	14.23			25.14	25.31	25.22
	16.00			28.23	28.30	28.26
	18.14			30.50	30.63	30.56
KOH	3.69			12.59	12.68	12.64
	6.25			13.65	13.55	13.60
	7.94		14.53	14.33	14.60	14.49
	11.36		16.00	16.17	15.98	16.05
	13.52			17.74	17.81	17.78

The heat evolved by the salt-alkali mixture was 11.50 cal. This is interesting since the heat evolved by an alkali solution of the same concentration but containing no sodium chloride was 12.18 cal.

TABLE II
 HEATS OF ADSORPTION OF VARIOUS SOLUTIONS BY STANDARD CELLULOSE

Reagent	Individual determinations, calories per gram cellulose		Mean, cal. per gm.
(a) Water	10.20	10.18	10.19
(b) NaCl soln. (16.6% wt.)	10.02	10.12	10.07
(c) NaCl-NaOH (16.6% + 2.81%)	11.53	11.47	11.50
(d) NaOH (2.81%-curve)			12.18
(e) K ₂ CO ₃ soln. (3.1% wt.)			10.32
(f) K ₂ CO ₃ soln. (14.7% wt.)			10.20

The concentrated sodium chloride solution gives a value somewhat less than that of water, the strong carbonate a value much the same as that of water, and the weaker carbonate solution a value higher than that of water. These facts, as well as the rest of the results given in Tables I and II, merit discussion.

Discussion

It was pointed out in the introduction that determinations of the heats of adsorption of sodium hydroxide by cotton cellulose were made by Neale. In Table III a comparison is made of the values he obtained in the same concentration range with those obtained here. The agreement of the results with solutions of 10.70 and 15.20% concentration is excellent.

 TABLE III
 A COMPARISON OF NEALE'S VALUES AND THE AUTHORS' FOR HEATS OF ADSORPTION OF SODIUM HYDROXIDE BY COTTON CELLULOSE

Sodium hydroxide, percentage by weight	8.08	10.70	13.90	15.20
Neale's values, calculated to present basis, cal.	12.92	16.85	25.72	27.84
Present values (curve), cal.	14.50	16.90	24.80	27.82

In Neale's determinations the cellulose was first permitted to adsorb the vapor (water) of the alkali solution before the reaction heat was measured. By the use of vapor pressure data (10, pp. 370 and 373), Argue and Maass's heat of adsorption data (1), and Walker's sorption isotherms (18), it was possible to recalculate Neale's measurements to the same basis as that of the present values.

Neale considered that all the heat of reaction was evolved in five minutes. In the present investigation it was observed that, although most of the heat was given out in the first three or four minutes, at least 25 or more minutes was required for all the heat to be evolved.

With soda-boiled cotton and a solution of 2.99 moles of sodium hydroxide per 1000 gm. of water, Neale's results (14, p. 389) varied from 1.18 to 1.30 kg-cal. per mole of cellulose, or from 7.28 to 8.02 cal. per gm. of cellulose. The largest variation in the present work, which occurred at the beginning

of the investigation on alkalis, was with 0.95% sodium hydroxide solution. For the four determinations at this concentration, the results varied from 11.17 to 11.49 cal. per gm. of cellulose. In all other determinations the variation was usually much less than 0.3 cal. It may be concluded that the present work affords the most accurate calorimetric data on alkali adsorption by cellulose to date.

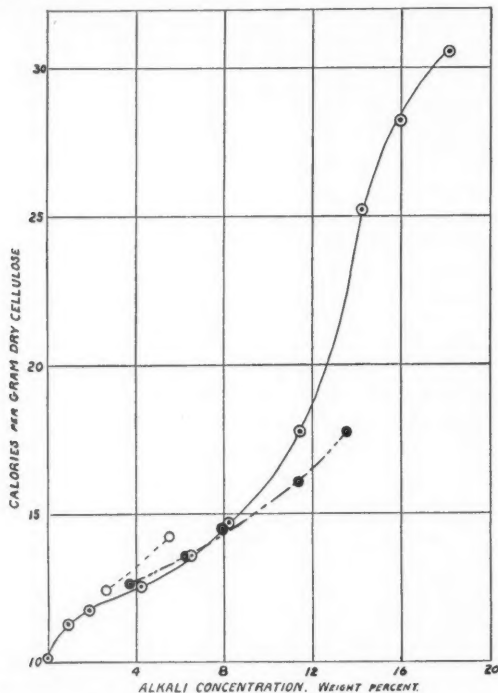


FIG. 1. Heat of adsorption of alkalis by cotton cellulose. \circ , Lithium hydroxide; \odot , sodium hydroxide; \bullet , potassium hydroxide.

The amount of alkali sorbed by cellulose has been determined by a large number of investigators. The results of Heuser and Bartunek (9) may quite profitably be considered, since they determined the relative adsorptions of several alkalis, including the three considered here. A relation between the amount sorbed and the heat evolved was sought by comparing Heuser and Bartunek's data with the thermal data. In Figs. 1 and 2 are plotted the heats evolved and the amounts adsorbed, respectively, for different percentages by weight of the three alkalis, lithium, sodium, and potassium hydroxides. The similarity in regard to the relative positions of the two sets of curves is striking. It would appear that the heat evolved is some measure of the amount of substance adsorbed.

Measurements of the amount of substance adsorbed have always been attended with experimental difficulties, and reference to the literature will show that the results of different investigators vary widely. The accuracy of the heat measurements as made by means of the adiabatic calorimeter is such that one may consider measurements of this type a more accurate measure of the amount of material adsorbed.

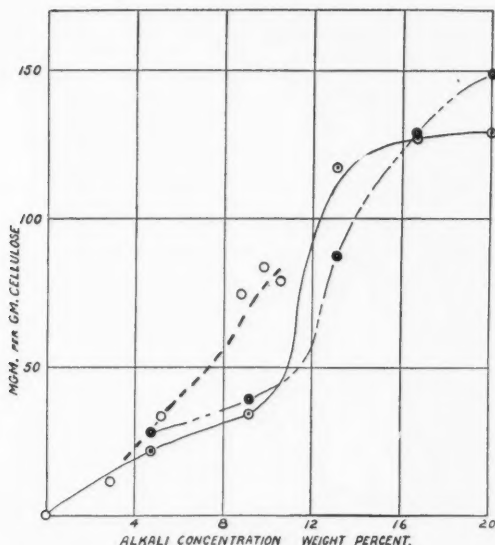


FIG. 2. Adsorption of alkalis by cotton cellulose (Heuser and Bartunek). \circ , Lithium hydroxide; \odot , sodium hydroxide; \bullet , potassium hydroxide.

The question arises whether the adsorption is molecular or ionic, or of some other type. Many investigators have postulated cellulose adsorption compounds of the type (cellulose)sodium hydroxide, etc., implying a molecular adsorption. It would appear from the order of the heats of adsorption, when plotted on a molar basis as in Fig. 3, and also from the comparison of weight values with those of Heuser and Bartunek, that it may be molecular. That is, compounds of higher molecular weights give higher heats of adsorption. But the differences, though greater than experimental error, are too small to be accounted for on this basis. On the molar basis (Fig. 3) the curves of heats of adsorption of sodium hydroxide and lithium hydroxide are nearly overlapping, yet the molecular weights of these compounds are 24 and 40. Some other explanation is therefore required.

Neale supplies a clue to the possible explanation. From his investigations (14) he concludes that cellulose in the presence of a strong base acts as a weak acid, yielding small amounts of H^+ ion. These H^+ ions presumably

come from the hydroxyl groups known to be present in cellulose. His hypothesis is that these H^+ ions neutralize the OH^- ions of the base to form water, and the alkali cation attaches itself to the oxygen of the cellulose much in the same manner as in salt formation. The cellulosate is very sensitive to hydrolysis, so that the presence of water virtually keeps it dissociated. The present results will now be discussed in the light of this hypothesis.

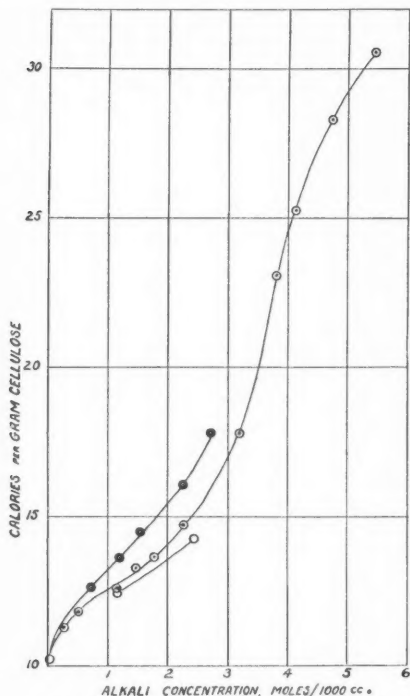


FIG. 3. Heat of adsorption of alkalis by cotton cellulose. \circ , Lithium hydroxide; \odot , sodium hydroxide; \bullet , potassium hydroxide.

tions would explain the variations in the quantity of heat evolved.

Further evidence based on the shape of the curves of heat of adsorption supports Neale's speculations. At first there is a rapid increase in the amount of heat evolved, then a slowing at about 5% (by weight) concentration. Two processes may cause this. Ordinary swelling, by increasing the surface, may make available an increased number of H^+ ions from the cellulose; but as maximum swelling is approached these H^+ ions become used up and a slowing of the neutralization process may occur. Also, the OH^- ion concentration due to the alkali does not increase as fast as does the molecular concentration. Both phenomena may be taking place simultaneously. After the slowing of

It has already been pointed out that two phenomena may be noted in regard to the evolution of heat when the results are plotted on a molar basis. The magnitudes of the heats evolved are similar for the three alkalis, and, at the same time, there is a well defined order of these magnitudes, namely, for lithium hydroxide, sodium hydroxide, and largest, potassium hydroxide. The strengths of these alkalis are quite similar, yielding a similar OH^- ion concentration. But the cations are hydrated in the order, Li^+ , Na^+ , and least, K^+ . A plausible explanation would be that the hydration of the cation influenced the availability of the OH^- ion. The most hydrated Li^+ ion would partly prevent its OH^- from forming water with the hydrogen from the weakly acidic cellulose. Further, the ease with which the cation could attach itself to the cellulose, subsequent to the neutralization process, would be influenced in the same direction by hydration. These considera-

the process there is a very rapid increase in the amount of heat evolved, and then a decrease (sodium hydroxide, Fig. 3). It is known that a drastic change occurs, beginning when the sodium hydroxide concentration is 10% (weight). A whole new surface is opened up and a superabundance of H^+ ions may now be made available; this would account for the large increase in heat evolution. But again, the new surface is used up, and a slowing of the process occurs when the concentration is greater than 15%.

It may be noted here that the rapid rise in the heat evolved at concentrations higher than 10% is even more pronounced than is apparent in Fig. 3. In another paper it will be shown that the heat of mercerization, the heat involved in the drastic change of the structure of cellulose at mercerizing strengths of alkalis, is endothermic. Consequently, the true adsorption heat is even larger than it appears, and an even steeper curve results.

Still further evidence for this (and Neale's) mechanism is supplied by the data regarding heats evolved when various salt solutions and a salt-alkali solution react with cellulose. With ordinary strong sodium chloride solution ((b), Table II) in which there is certainly a superabundance of Na^+ ions, the heat evolved is slightly less than that when water alone is used. Apparently, sodium chloride is not adsorbed appreciably by cellulose; it probably only competes with cellulose for water. Its influence, in depressing the amount of heat evolved, as compared with that evolved in water alone, may be called a "bulk" effect, reducing the water concentration.

The heat evolved in a solution containing sodium hydroxide (2.81%) and the same amount of sodium chloride as that in the solution mentioned above (16.6%) ((c), Table II) is considerably less than that given out in a solution of the same alkali concentration but containing no sodium chloride. Moreover, the difference is much more than can be accounted for by the "bulk" effect that sodium chloride exhibits. The only explanation seems to be that the OH^- ion concentration is affected. The presence of an excess of Na^+ ions increases the amount of molecular sodium hydroxide, but decreases the availability of OH^- ions. Two conditions appear to be evident; (i) the adsorption phenomenon is probably not molecular, and (ii) the availability of OH^- ions seems to be of prime importance in the adsorption process.

The results obtained with potassium carbonate solutions provide only further support for these ideas. The heat evolved in a solution of low concentration is measurably greater than that in water alone. It is well known that a solution of this salt has an excess OH^- concentration, and, though small, it is apparently sufficient to form water from the H^+ ions of the very weakly acidic cellulose. On the other hand, the heat given out in a concentrated carbonate solution is the same as that in water. Apparently, the "bulk" effect of the salt in the water solution balances the effect of the OH^- ion concentration.

It has been considered that the evolution of heat is due to the ionization of very weakly acidic cellulose, and to the subsequent processes of water formation and alkali cation adsorption. But it cannot be said how much is contributed by any of these processes.

Very recently Bancroft and Calkin (2) published what they considered was the most accurate measure of the amount of adsorption of sodium hydroxide by cellulose. It is of interest to compare their results with those of

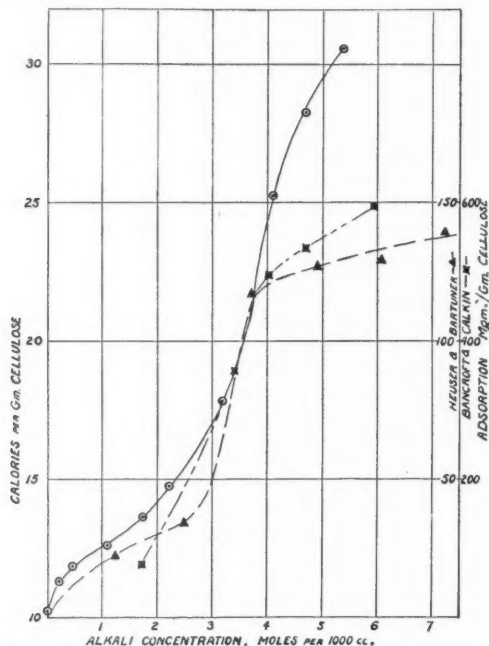


FIG. 4. Comparison of heat of adsorption with amount of adsorption of sodium hydroxide by cellulose.

Heuser and Bartunek, and with the present thermal data, as in Fig. 4. The first portion of Heuser and Bartunek's curve seems to follow very closely the variations of the curve of heat evolved.

References

1. ARGUE, G. H. and MAASS, O. *Can. J. Research*, 12 : 564-574. 1935.
2. BANCROFT, W. D. and CALKIN, J. B. *J. Phys. Chem.* 39 : 1-9. 1935.
3. BARRATT, T. and LEWIS, J. W. *J. Textile Inst.* 13 : 113-120. 1922.
4. BERTETTI, J. W. and McCABE, W. L. *Ind. Eng. Chem.* 28 : 375-378. 1936.
5. CHILIKIN, M. M. *Zhur. Priklad. Khim.* 3 : 221-230. 1930; *Chem. Abstr.* 24 : 3899. 1930.
6. COWARD, H. F. and SPENCER, L. *J. Textile Inst.* 14 : T28-T32. 1923.
7. GUCKER, F. T. and SCHMINKE, K. H. *J. Am. Chem. Soc.* 54 : 1358-1378. 1932.
8. GUCKER, F. T. and SCHMINKE, K. H. *J. Am. Chem. Soc.* 55 : 1013-1019. 1933.
9. HEUSER, E. and BARTUNEK, R. *Cellulosechem.* 6 : 19-26. 1925.
10. INTERNATIONAL CRITICAL TABLES. McGraw-Hill Book Company, New York. Vol. 3. 1928.
11. JOYNER, R. A. *J. Chem. Soc. Trans.* 121 : 2395-2409. 1922.
12. LEIGHTON, A. *J. Phys. Chem.* 20 : 32-50. 1916.
13. MORRISON, J. L., CAMPBELL, W. BOYD, and MAASS, O. *Can. J. Research, B*, 15 : 447-456. 1937.
14. NEALE, S. M. *J. Textile Inst.* 20 : 373-400. 1929.
15. VIEWEG, W. *Ber.* 40 : 3876-3883. 1907.
16. VIEWEG, W. *Ber.* 41 : 3269-3275. 1908.
17. VIEWEG, W. *Ber.* 57 : 1917-1921. 1924.
18. WALKER, F. Ph.D. Thesis. McGill University. 1937.

THE REACTION OF OXYGEN ATOMS WITH METHANE¹

By E. W. R. STEACIE² AND N. A. D. PARLEE³

Abstract

The reaction of oxygen atoms, produced by the discharge tube method, with methane has been investigated at temperatures from 30° to 330° C. The products of the reaction are carbon monoxide, carbon dioxide, and water. Ethane is absent. The activation energy is approximately 8 Kcal. It is concluded that either

(a) The reaction postulated by Norrish



does not occur to any great extent, or

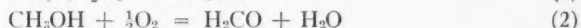
(b) The reaction



has an activation energy greater than 11 to 12 Kcal.

Introduction

There is considerable uncertainty regarding the theoretical basis of the oxidation reactions of the hydrocarbons. According to the hydroxylation theory, which was proposed by Bone (3), and has been mainly upheld by him and his co-workers, the fundamental reactions in the oxidation of methane are



The peroxidation theory (4) assumes, on the other hand, that the first stage in oxidation reactions is the formation of an unstable peroxide which initiates chain processes by means of which reactivity is handed on from the active products (peroxides) to the reactant molecules.

Neither of these theories is wholly satisfactory, and Norrish (10) has suggested a theory which is somewhat of a compromise between the other two. He suggests that the initial steps in the oxidation of methane are:



thus setting up chain processes in which the carriers are methylene radicals and oxygen atoms.

If Norrish's assumptions are correct, then it should be possible, by the Wood-Bonhoeffer method, to cause Reaction (3) to occur to a large extent by introducing atomic oxygen in high concentration into methane. If under these circumstances Reaction (3) occurs largely, then in addition to Reaction (4) there is also the possibility of



No direct information is available as to the rate of Reaction (5), but its occurrence has been suggested by Kassel (7) as a step in the decomposition

¹ Manuscript received April 5, 1938.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

² Associate Professor of Chemistry, McGill University.

³ Holder of a studentship under the National Research Council of Canada.

of methane. Kassel suggests a mechanism for the methane decomposition which fits the experimental data excellently. The arguments on which this mechanism is based lead to the conclusion that Reaction (5) has the high activation energy of 44 Kcal. Of course, a successful mechanism is not necessarily unique, and the evidence that E_5 is 44 Kcal. is thus rather speculative.

Belchetz and Rideal (1, 2) investigated the primary split of methane into radicals at high temperatures and concluded that the primary reaction was



On the other hand, Rice and Dooley (11, 12), using the Rice technique, were unable to detect the methylene radical, and found only methyl radicals in the methane decomposition. They consider the primary split to be



They also discuss the possibility of the methyl radicals having been formed by secondary processes. If this is so, then the absence of methylene radicals in their experiments must be ascribed to either Reaction (5) or



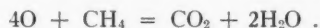
being fast enough to keep the concentration of methylene radicals down to a low value. They show that for this to occur either Reaction (8), or more likely Reaction (5), would have to have an activation energy less than 12 Kcal., which they consider to be too low.

The consensus of opinion is thus that Reaction (5) has a high activation energy. However, the evidence is very uncertain, and it appeared to be possible that Reaction (5) was a rapid reaction, and that the discrepancy between the work of Rice and Dooley and that of Belchetz and Rideal might be ascribed to its occurrence.

It follows that if the primary step in the methane oxidation is that postulated by Norrish, as appears likely, then there is the possibility of ethane formation by Reaction (5). If this were found to be the case it would lend support to the Norrish mechanism, and at the same time approximately define the activation energy of Reaction (5). If no ethane were found, the result would be somewhat inconclusive, since its absence could be due to the non-occurrence of either Reactions (3) or (5). It appeared, however, to be worth investigating the possibility of the occurrence of ethane in the reaction of oxygen atoms with methane.

The reaction of oxygen atoms with methane has been investigated by Harteck and Kopsch (6). They used the usual Wood-Bonhoeffer type of apparatus, and froze the condensable products out of the flowing stream by means of a liquid air trap. With this method the only condensable products were carbon dioxide and water, since carbon monoxide and ethane would have passed through the trap and been lost. They found more water than

carbon dioxide, approximately in the ratio of 2 : 1 by weight, instead of 1 : 1.22 as required if the reaction went completely by



They therefore concluded that carbon monoxide was formed as well. From the water formed they calculated the following percentage oxidation of methane in various experiments. The oxygen atom concentration in these experiments was approximately 30%.

Temperature, °C.	30	100	189
Percentage of methane reacted	1.0, 0.9, 1.1	2.1, 2.0	5.9, 6.5

The carbon dioxide formed in these experiments must have come from some intermediate product, such as formic acid, since the oxidation of carbon monoxide by oxygen atoms is quite slow. The results indicated an activation energy for the reaction of approximately 7 Kcal. (5).

Experimental

The apparatus was essentially the same as that used by one of us in previous investigations of hydrogen atom reactions (13, 14).

The discharge was operated with an applied voltage of about 3500 across the tube and a 5000 ohm resistance. The current was maintained at 320 milliamperes by means of a rheostat in the primary of the transformer. The reaction chamber had a diameter of 7 cm. and a length of 70 cm., and was surrounded by an electric furnace which could be slipped up and down the tube to permit observation when the efficiency of wall poisoning, etc., was being tested. Two tubes entered the reaction vessel from below, one of which contained a thermocouple; the other served as an inlet for methane.

In these experiments no attempt was made to measure the oxygen atom concentration, since the main purpose of the investigation was the determination of the products of the reaction. However, from the intensity of the afterglow, as compared with previous observations of the same kind with known oxygen atom concentrations, it was approximately 20% at room temperature. The uncertainty in this value is certainly less than a factor of 2.

The walls of the apparatus were poisoned by rinsing with a 5% solution of phosphoric acid in the usual way.

Tank oxygen was used. It contained no appreciable impurity other than a small amount of nitrogen and the rare gases. The oxygen was admitted to the discharge through a calibrated capillary flowmeter.

Methane was secured in cylinders from the Ohio Chemical and Manufacturing Co. It was purified by distillation and stored in a large reservoir. In making an experiment it was expanded into two successively smaller reservoirs of known volume. The smaller of these volumes was connected

to the apparatus through a capillary flowmeter. By adjusting the pressure in the smaller reservoir it was possible to secure any desired rate of flow, and by observing the change in pressure in the secondary storage volume the amount of gas used could be accurately calculated.

After leaving the reaction vessel the gas passed through a trap at -80°C . in order that easily condensable products would be removed, and then through the high-speed diffusion pump. After leaving the pump the gas passed through a large trap at -183°C . which contained silica gel. This served to remove methane and other low-boiling gases. The residual gas then went to an oil pump.

At the end of an experiment the silica gel trap was allowed to warm up, and the gas was desorbed and expanded into a large storage volume. The last of the adsorbed gas was removed with a Toepler pump and pumped into the same volume, and the total volume of recovered gas was then measured. Blank runs showed that all the methane and about 85% of the oxygen were trapped by the gel. It was safe, therefore, to assume that all gases with boiling points higher than that of methane would be completely recovered. On account of its comparatively small amount, carbon monoxide was also completely recovered. (It should be noted that in spite of its slightly lower boiling point, carbon monoxide is more strongly adsorbed by silica gel than is oxygen (9).)

Analyses of the gaseous products were made in a Burrell gas analysis apparatus for oxygen, carbon dioxide, unsaturated hydrocarbons, carbon monoxide, and saturated hydrocarbons. The hydrocarbon fraction of the reaction products was analyzed in a low-temperature fractional distillation apparatus of the Podbielniak type. As large quantities of oxygen interfered with the distillation, it was necessary to remove oxygen before the distillation. It was also necessary to remove carbon dioxide since it sublimates at atmospheric pressure. These gases were therefore removed prior to the distillation by shaking the sample with a sodium-hydrosulphite-potassium-hydroxide solution.

Experimental Results

The Products of the Reaction

The products of the reaction at various temperatures are given in Table I. It will be seen from the table that the amount of carbon dioxide formed is in good agreement with the findings of Harteck and Kopsch. Harteck and Kopsch could not determine carbon monoxide with their experimental arrangement, and they therefore inferred its amount from the water formed. Our results indicate a considerably greater formation of carbon monoxide than that inferred by them. This is possibly due to the adsorption of water on the walls, which may have cut down the observed water formation in their work. In our case, water could not be determined since the walls of the apparatus were poisoned with a solution of phosphoric acid. Part of the discrepancy is also due to the fact that we used a larger reaction vessel, and hence the contact time in our work was greater than in theirs. They did not calculate collision

yields from their experiments, so that the latter point cannot be directly verified. Geib (5), however, has estimated an activation energy of 7 Kcal. from their work which would indicate a collision yield very similar to that obtained by us. The two investigations may therefore be considered to be in satisfactory agreement.

TABLE I
THE PRODUCTS OF THE REACTION
(See Table II for pressures, flow rates, etc.)

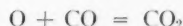
Run No.	Temperature, °C.	Methane used, cc.	Ratio O ₂ /CH ₄	Percentage CH ₄ converted to			Total percentage reaction
				CO	CO ₂	C ₂ H ₆ or heavier	
1	37	415	4.0	10.5	—	None	10.5
2	200	550	4.0	27.1	5.7	None	32.8
3	201	608	4.0	28.1	7.3	None	35.4
4	303	697	4.0	33.4	21.9	None*	55.3
5	330	490	4.0	30.2	19.2	None*	49.4
6	315	700	4.0	31.3	19.7	None*	51.0

* Combustion analyses of the hydrocarbon fraction from Runs 4, 5, and 6 confirmed the absence of ethane.

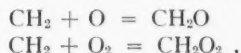
It is significant that no appreciable quantity of formic acid, formaldehyde, or any other intermediate oxidation product is formed. This leads to the conclusion that the primary reaction of oxygen atoms with methane is slow compared with the later steps which continue until the methane has been completely oxidized to carbon monoxide, carbon dioxide, and water. This slow primary step may well be that suggested by Norrish



Since the reaction



is comparatively slow (6), the carbon dioxide formed cannot have resulted from the oxidation of carbon monoxide, at least at room temperature. It seems probable therefore that the next steps in the oxidation may be



and that these are followed by the oxidation of formaldehyde and formic acid. It has been shown by Geib (5) that the reaction of oxygen atoms with formaldehyde yields mainly carbon monoxide, while formic acid yields mainly carbon dioxide. Both reactions are rapid at room temperature, the activation energies being below 7 Kcal.

The absence of ethane or other saturated hydrocarbons leaves the evidence for the Norrish mechanism inconclusive, since we have the alternative possibilities:

(a) The reaction



TABLE II
REACTION OF METHANE WITH OXYGEN ATOMS
Atom concentration, assumed 20%; volume of reaction vessel, 1370 cc.

Run No.	Temperature, °C.	Pressure, mm.	Methane flow, cc./sec., at N.T.P.	Oxygen flow, cc./sec., at N.T.P.	Total flow cc./sec., at experimental conditions (corrected for presence of atoms)	Reaction time, sec.	Partial pressure of oxygen atoms, cm.	No. of collisions per sec. by one CH ₄ molecule with oxygen atoms	No. of collisions by one CH ₄ molecule with oxygen atoms in reaction time	Percentage reaction	Collision yield	Activation energy, Kcal., on assumption of a steric factor of 0.1
1	37	0.32	0.0628	0.250	919	1.49	0.0052	3.58×10^6	5.33×10^6	10.5	1.98×10^{-7}	8.1
2	200	0.34	0.0628	0.254	1334	1.03	0.0055	3.06×10^6	3.14×10^6	32.8	1.04×10^{-6}	10.8
3	201	0.33	0.0632	0.248	1350	1.01	0.0054	3.00×10^6	3.03×10^6	35.4	1.17×10^{-6}	10.7
4	303	0.33	0.0630	0.254	1678	0.82	0.0055	2.77×10^6	2.26×10^6	55.3	2.44×10^{-6}	12.1
5	330	0.35	0.0632	0.250	1639	0.84	0.0057	2.83×10^6	2.36×10^6	49.4	2.09×10^{-6}	12.9
6	315	0.32	0.0630	0.248	1732	0.79	0.0053	2.64×10^6	2.09×10^6	51.0	2.44×10^{-6}	12.4

does not occur, or

(b) The reaction



is not a rapid reaction, its activation energy being greater than 11 to 12 Kcal., and hence the absence of methylene radicals in Rice and Dooley's work cannot be ascribed to its occurrence. However, it must be admitted that the situation is too complex to admit of very definite conclusions.

The Kinetics of the Reaction

Although this investigation was made primarily for the purpose of determining the products of the reaction of oxygen atoms with methane, the results are sufficiently detailed to enable an estimate of the activation energy of the process to be made as well. The data on which this estimate is based are given in Table II, an atom concentration of 20% being assumed,

$$\text{i.e., } \frac{P_o}{P_o + P_{O_2}} = 0.20 .$$

It will be seen that the collision yield at room temperature leads to an activation energy of 8.1 Kcal., which is in satisfactory agreement with Geib's approximate estimate of 7 Kcal. from the results of Hardeck and Kopsch.

The activation energies calculated from the collision yields at higher temperatures are considerably higher than this value. This is undoubtedly due to the fact that the atom concentration at higher temperatures is much less than that at room temperature, since the efficiency of the wall poisoning diminishes rapidly as the temperature is raised. If we assume that the atom concentration at 300° has fallen to about 2%, the activation energies calculated from experiments at higher temperatures are brought into line.

References

1. BELCHETZ, L. Trans. Faraday Soc. 30 : 170-179. 1934.
2. BELCHETZ, L. and RIDEAL, E. K. J. Am. Chem. Soc. 57 : 1168-1174. 1935.
3. BONE, W. A. and TOWNEND, D. T. A. Flame and combustion in gases. Longmans, Green and Co. London. 1927.
4. EGERTON, A. Nature, 121 : 10. 1928.
5. GEIB, K. H. Ergeb. exakt. Naturw. 15 : 44-105. 1936.
6. HARTECK, P. and KOPSCH, U. Z. physik. Chem. B, 12 : 327-347. 1931.
7. KASSEL, L. S. J. Am. Chem. Soc. 54 : 3949-3961. 1932.
8. KASSEL, L. S. J. Am. Chem. Soc. 57 : 833-834. 1935.
9. MCBAIN, J. W. The sorption of gases and vapours by solids. George Routledge and Sons, Ltd., London. 1932.
10. NORRISH, R. G. W. Proc. Roy. Soc. Lond. A, 150 : 36-57. 1935.
11. RICE, F. O. J. Am. Chem. Soc. 56 : 488-490. 1934.
12. RICE, F. O. and DOOLEY, M. D. J. Am. Chem. Soc. 55 : 4245-4247. 1933.
13. STEACIE, E. W. R. Can. J. Research, B, 15 : 264-273. 1937.
14. STEACIE, E. W. R. J. Chem. Phys. 6 : 37-40. 1938.

THE POLYMERIZATION OF ISOBUTENE¹By E. W. R. STEACIE² AND G. SHANE³

Abstract

An investigation of the polymerization of isobutene has been made at low temperatures and pressures, using very small percentage conversions. The reaction rate curves are pronouncedly autocatalytic in nature, and the process appears to be too complex to yield very much information concerning the kinetics of the reaction.

Introduction

Most of our knowledge of the polymerization reactions of the higher olefins comes from the work of Krauze, Nemtsov, and Soskina (2-6), who have investigated the polymerization of ethylene, propene, the butenes, and pentene at high pressures in the temperature range 300° to 400° C. The reactions are all second order, the products being mainly, but not exclusively, those corresponding to a straight association to give an olefin with twice the number of carbon atoms. The kinetic constants, together with collision efficiencies calculated by Bawn (1), are given in Table I.

TABLE I

Reaction	<i>E</i> , Kcal.	log ₁₀ <i>A</i>	Collision efficiency
2C ₂ H ₄ = C ₄ H ₈	37.7	10.8	4 × 10 ⁻³
2C ₃ H ₆ = C ₆ H ₁₂	37.4	10.2	1 × 10 ⁻³
2C ₄ H ₈ = C ₈ H ₁₆	38.0	10.0	5 × 10 ⁻⁴
2 <i>iso</i> -C ₄ H ₈ = C ₈ H ₁₆	43.0	12.3	1 × 10 ⁻¹
2C ₅ H ₁₀ = C ₁₀ H ₂₀	38.0	9.8	4 × 10 ⁻⁴

It will be seen that, with the exception of the values for isobutene, *A*, *E*, and the collision efficiency are almost the same for all members of the series. The difference in the case of isobutene is of considerable interest, if real. However, the fact that both *A* and *E* alter in such a way as to compensate each other makes the result open to considerable suspicion. Also, a collision efficiency as great as 1/10 is very unlikely for an association reaction. It therefore seemed of interest to reinvestigate the polymerization of isobutene.

Experimental

Previous work on the olefin polymerizations has been done at high pressures, to swamp out the accompanying first order decomposition reactions. It was decided in the present work to use low pressures and very small conversions, and to follow the reaction by determining the diisobutene formed. In this way it was hoped to avoid complications due to the decomposition, and at the same time be able to work at low pressures where greater accuracy is attainable.

¹ Manuscript received April 14, 1938.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.

² Associate Professor of Chemistry, McGill University.

³ Graduate Student, Department of Chemistry, McGill University.

The method of following the progress of the reaction was as follows. Gaseous isobutene was admitted to a Pyrex bulb in an electric furnace at a measured pressure. After the lapse of a predetermined time, the contents of the reaction vessel was pumped out through a liquid air trap. The trap was then warmed to -80°C . and the unreacted isobutene was pumped away until the pressure had fallen to 0.001 mm. The contents of the trap was then evaporated, recondensed, and the trap again pumped down. The diisobutene was then re-evaporated into a known volume, and its pressure measured on an oil manometer.

Isobutene was prepared by refluxing a mixture of tertiary butyl alcohol and anhydrous oxalic acid. The resulting gas was condensed and fractionally distilled several times. A further distillation through a Podbielniak column indicated no appreciable amount of impurity.

The diisobutene from a large number of runs was collected, and this aggregate, amounting to about 1 cc., was distilled through a small column of the Podbielniak type. It gave a boiling range of 100° to 107°C . at 760 mm. pressure, in good agreement with the results of Whitmore and Wrenn (7) who found a boiling range of 100° to 105°C . for a mixture of the isomeric diisobutenes. The vapor pressure of the product was 37 mm. at 25°C . Its refractive index was $n_D^{20} = 1.422$, as compared with 1.408 to 1.415 found by Whitmore and Wrenn for the various isomers of diisobutene.

Results

The results obtained were complex. Those from a set of runs at 60 cm. initial pressure are given in Fig. 1. The pronounced "auto-catalytic" nature of the reaction-time curves is noteworthy. As a consequence of this the interpretation of the results is difficult and very great accuracy cannot be expected. The only feasible way to treat the experimental data is to overlook all but the initial rates, *i.e.*, those before the "breaks" in the curves occur. It is found that in this region the reaction is fairly accurately second order, in so far as the effect of varying initial concentration on the initial rate is concerned. The reaction is influenced by the surface to some extent, runs in a packed vessel indicating from 6 to 20% heterogeneity. It was also found that,

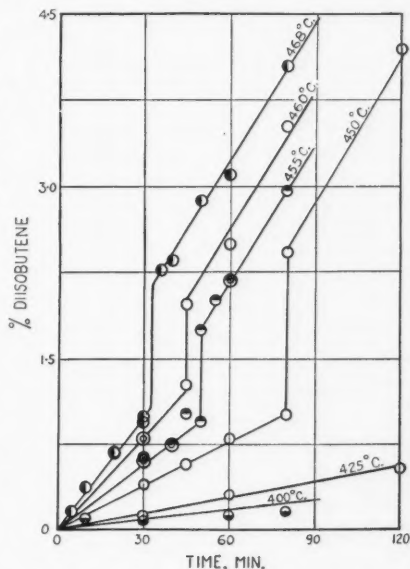


FIG. 1. The rate of polymerization of isobutene. Initial pressure, 60 cm. The rates are expressed as percentage of diisobutene formed in terms of the initial amount of isobutene.

as in the ethylene polymerization, small amounts of oxygen had a pronounced catalytic effect. Thus in one experiment at 400° C., 2 mm. of oxygen added to 60 cm. of isobutene increased the rate by a factor of 4.

In view of these complications, no very accurate kinetic data could be obtained. However, the temperature coefficient of the initial rate, plotted in the form of a curve of log rate against $1/T$, gave a fairly good straight line and indicated an activation energy of 43.4 Kcal., with an uncertainty of perhaps 3 to 4 Kcal. This value is in excellent agreement with the results of Krauze *et al.* From this we get for the initial rate constant

$$\log_{10} k = 9.65 - \frac{43400}{2.3RT} \text{ litre mol.}^{-1} \text{ sec.}^{-1}$$

It is apparent, therefore, that while our value for the activation energy is in good agreement with the results of Krauze, Nemtsov, and Soskina, there is a very large difference in the A factor obtained from the two investigations. Our value is in line with those found for the other olefins, and as a result the collision efficiency calculated from our work is also in line with those of the other olefins, *viz.*, approximately 4×10^{-4} .

This discrepancy between the two investigations is primarily due to the fact that our absolute rates are much lower than those of Krauze *et al.* (by a factor of about 200). The fact that the reaction is partly heterogeneous cannot account for the discrepancy, since this means that our rates are somewhat *higher* than they should be. The real causes of the discrepancy would seem to be that (*a*) the reaction is not accurately second order, and hence our results cannot be properly compared with those obtained at very high pressures, and (*b*) the complex nature of the rate curves makes accurate interpretation impossible. In view of these facts it does not seem advisable to give much weight to the previously reported high collision efficiency of the reaction.

References

1. BAWN, C. E. H. Trans. Faraday Soc. 32 : 178-187. 1936.
2. KRAUZE, M. V., NEMTZOV, M. S. and SOSKINA, E. A. Compt. rend. acad. sci. U.R.S.S. 2 : 301-306. 1934.
3. KRAUZE, M. V., NEMTZOV, M. S. and SOSKINA, E. A. Compt. rend. acad. sci. U.R.S.S. 3 : 262-267. 1934.
4. KRAUZE, M. V., NEMTZOV, M. S. and SOSKINA, E. A. J. Gen. Chem. U.S.S.R. 5 : 343-355. 1935.
5. KRAUZE, M. V., NEMTZOV, M. S. and SOSKINA, E. A. J. Gen. Chem. U.S.S.R. 5 : 356-360. 1935.
6. KRAUZE, M. V., NEMTZOV, M. S. and SOSKINA, E. A. J. Gen. Chem. U.S.S.R. 5 : 382-387. 1935.
7. WHITMORE, F. C. and WRENN, S. N. J. Am. Chem. Soc. 53 : 3136-3142. 1931.

CONTRIBUTION TO THE STRUCTURE OF DISTYRENES¹BY LÉO MARION²

Abstract

Dehydration of $\alpha\gamma$ -diphenylbutyl alcohol with potassium bisulphate yields 1,3-diphenyl-3-butene which can be oxidized to β -phenylpropiophenone. This 3-butene isomerizes on standing to a crystalline 1,3-diphenyl-1-butene which forms a dibromo-derivative and gives benzaldehyde and hydratropic aldehyde when ozonized. If $\alpha\gamma$ -diphenylbutyl alcohol is dehydrated with 20% sulphuric acid, it also yields 1, 3-diphenyl-3 butene, but this isomerizes to 1,3-diphenyl-2-butene from which acetophenone is obtained on oxidation.

Staudinger's proof of the identity of the pyrolytic distyrene with 1,3-diphenyl-3-butene is not valid since $\alpha\gamma$ -diphenylpropane, present with the distyrene, produces β -phenylpropiophenone when oxidized.

When highly polymerized styrene is subjected to pyrolysis *in vacuo*, a partly depolymerized product is obtained. Recently Staudinger and Steinhofer (5) found that this product consists of a complex mixture of styrene, di-, tri-, and tetra-styrene together with saturated hydrocarbons. From the distyrene fraction, by catalytic polymerization of the ethylenic component, they succeeded in isolating $\alpha\gamma$ -diphenylpropane. On oxidizing the distyrene fraction they isolated β -phenylpropiophenone, and, on the basis of this result, attributed to the ethylenic component the structure of 1,3-diphenyl-3-butene. These experiments have since been repeated and confirmed by Midgley, Henne, and Leicester (4). The properties exhibited by 1,3-diphenyl-3-butene, as will appear from the sequel, and the impossibility of isolating any crystalline dibromide from pyrolytic distyrene led the present author to doubt the validity of Staudinger and Steinhofer's interpretation of their results. A reconsideration of the oxidation of pyrolytic distyrene suggested a different interpretation. It is well known that paraffins substituted by one or more phenyl groups can be oxidized to ketones (2). Pure $\alpha\gamma$ -diphenylpropane was, therefore, oxidized under conditions identical with those used by Staudinger and Steinhofer, and found to give an excellent yield of β -phenylpropiophenone. Hence, the conclusion of Staudinger and Steinhofer that pyrolytic distyrene is 1,3-diphenyl-3-butene is based on a fallacious interpretation of their results.

It was thought that the identity of the ethylenic component of pyrolytic distyrene with 1,3-diphenyl-3-butene might be proved or disproved more readily by synthetic methods, and the latter compound has now been synthesized. The ethyl ester of $\alpha\gamma$ -diphenylbutyric acid (3) was reduced to the corresponding alcohol which was dehydrated either with potassium bisulphate or with sulphuric acid. Both methods of dehydration gave 1,3-diphenyl-3-butene (I) which is an unstable, colorless oil. When oxidized with potassium permanganate in acetone solution it yields the expected β -phenylpropiophenone (II).

¹ Manuscript received May 2, 1938.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

² Chemist, National Research Laboratories, Ottawa, Canada.

However, 1,3-diphenyl-3-butene rapidly isomerizes on standing. When it has been obtained by potassium bisulphate dehydration, it is transformed mainly into a crystalline isomer, m.p. 47° C.,* which can be ozonized to benzaldehyde and hydratropic aldehyde, and is, therefore, 1,3-diphenyl-1-butene (III). When the dehydration has been effected with sulphuric acid, 1,3-diphenyl-3-butene isomerizes chiefly to 1,3-diphenyl-2-butene (IV). The latter, on oxidation with potassium permanganate gives acetophenone.



1,3-Diphenyl-1-butene forms a well characterized crystalline dibromo-derivative, m.p. 86.5° C., from which the bromine can be removed and the crystalline hydrocarbon recovered. The latter is unstable and is slowly oxidized. Even when the hydrocarbon is kept in a stoppered bottle, the odor of benzaldehyde can soon be detected. From a consideration of its oxidation products, it is apparent that the crystalline hydrocarbon must have the structure III. Likewise, the formation of β -phenylpropiophenone from the freshly prepared dehydration product of $\alpha\gamma$ -diphenylbutyl alcohol makes it impossible to assign to this hydrocarbon any structure other than that of 1,3-diphenyl-3-butene (I). This is further supported by the failure of this hydrocarbon to crystallize on inoculation with the crystalline 1,3-diphenyl-1-butene, eventually obtained from it on standing, although it crystallizes immediately if inoculated after having stood for some time.

From cinnamic acid, Stoermer and Kootz (6) have prepared a liquid distyrene which produced benzoic acid and hydratropic aldehyde when oxidized, and is, therefore, a 1,3-diphenyl-1-butene. From this distyrene they isolated three crystalline dibromo-derivatives (m.p. 129°, 122°, and 79° C.). On repeating their work, the author isolated two dibromo-derivatives, both melting at 129° C. and melting at 102° C. when admixed, but has failed to obtain the third as a crystalline substance. Inoculation of the mother liquors from these two crystalline dibromo-derivatives with the dibromide of the crystalline isomer (m.p. 86.5° C.) failed to bring about crystallization. There seems to be no doubt that the dibromide melting at 86.5° C. is different from that melting at 79° C. Since 1,3-diphenyl-1-butene is capable of *cis-trans* isomerism and each of the isomers can form two dibromo-derivatives, it is probable that the crystalline hydrocarbon (m.p. 47° C.) is the *trans*-isomer, whereas the liquid distyrene of Stoermer and Kootz is the *cis*-compound. The dibromide, m.p. 86.5° C., described above, is thus the last missing dibromide of the four theoretically possible.

The dibromo-derivatives of the diphenylbutenes I and IV are oils which could not be crystallized.

*All melting points are corrected.

If pyrolytic distyrene is really 1,3-diphenyl-3-butene, then it should be possible, after bromination, to isolate from the product the crystalline dibromo-derivative, m.p. 86.5° C. of the isomeric 1,3-diphenyl-1-butene which is formed so readily from it. A polystyrene fraction of average molecular weight 8000 was pyrolyzed *in vacuo* according to the usual procedure and the distyrene fraction isolated. This, however, could not be induced to crystallize by inoculation with the crystalline 1,3-diphenyl-1-butene nor, after bromination, by inoculation with the dibromo-derivative of m.p. 86.5° C.

Experimental

Preparation of $\alpha\gamma$ -Diphenylbutyric Acid

This was best prepared by the method of Kohler and Kimball (3) from α -phenyl- β -benzoylpropionic acid by a Clemmensen reduction. The acid can also be prepared from diethyl *sodio*-phenylmalonate and phenylethylbromide in absolute alcohol. The phenyl-phenylethylmalonic ester produced is saponified, and the acid when distilled *in vacuo* yields $\alpha\gamma$ -diphenylbutyric acid which, recrystallized from petroleum ether, forms beautiful prismatic crystals, m.p. 75° C. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.66%. Found: C, 79.98; H, 6.70%.

Preparation of $\alpha\gamma$ -Diphenylbutyl Alcohol

$\alpha\gamma$ -Diphenylbutyric acid is esterified and the ester reduced by Bouveault's method with sodium and alcohol to $\alpha\gamma$ -diphenylbutyl alcohol (90% yield). The alcohol is a colorless, viscous oil, b.p. 174° to 180° at 1 mm.

Dehydration of $\alpha\gamma$ -Diphenylbutyl Alcohol with Potassium Bisulphate

The alcohol was heated for one hour with potassium bisulphate and distilled under diminished pressure, b.p. 140° C. at 2 to 3 mm. This hydrocarbon is a colorless, fairly mobile oil. A sample (1 gm.) of the hydrocarbon was dissolved in acetone and treated at room temperature with potassium permanganate added in small portions, each equivalent to half an atom of oxygen. A total of 3.5 atoms was required. The product yielded benzoic acid and a neutral oil which crystallized on standing. Recrystallized from petroleum ether, it melted at 75° C. Admixed with an authentic sample of β -phenylpropiophenone of m.p. 74° C., the mixture melted at 74° C. The ketone was converted into the oxime which, recrystallized from petroleum ether, melted at 87° to 88° C. Admixture with β -phenylpropiophenone-oxime failed to depress the melting point.

Bromination of 1,3-Diphenyl-3-butene

The hydrocarbon obtained as described above (7.7 gm.) was dissolved in chloroform, and after cooling was treated with a chloroformic solution of bromine. After the solution had stood one hour at room temperature, the excess bromine and the chloroform were evaporated under reduced pressure, and the residual oil was dissolved in boiling methanol. On cooling, the solution deposited a crop of crystals which, after one recrystallization from methanol, melted at 86.5° C. (yield, 2.6 gm.) Calcd. for $C_{16}H_{16}Br_2$: Br, 43.44%. Found, 43.66, 43.46%.

Isolation of 1,3-Diphenyl-1-butene

The crystalline dibromo-derivative, when digested with zinc dust in alcohol, yields an oil, b.p. 130° to 140° C. at 1 mm., which crystallized on cooling. Recrystallized from methanol, m.p. 47° to 47.5° C. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.68%. Found: C, 91.30, 91.50; H, 7.65, 7.59%. The crystalline hydrocarbon, when rebrominated, yields the crystalline dibromide, m.p. 86.5° C.

Some of the original 1,3-diphenyl-3-butene which had not been brominated, but had been kept for some time, was inoculated with a crystal (m.p. 47° C.), whereupon it immediately deposited crystals, which, filtered from the accompanying oil and recrystallized, were identical with the hydrocarbon obtained from the dibromo-derivative.

The crystalline hydrocarbon (0.3 gm.) was ozonized in chloroform solution, and the ozonides were decomposed by boiling for 45 min. with water, zinc dust, and a trace of hydroquinone. The product, which had a strong odor of benzaldehyde, yielded two semicarbazones, m.p. 222° to 223° and m.p. 147° to 148° C. The first when admixed with benzaldehyde-semicarbazone (m.p. 229° C.) melted at 226° C.; the other, admixed with hydratropic aldehyde-semicarbazone (m.p. 154° C.) melted at 151° C. The hydrocarbon was also oxidized with permanganate, whereupon it yielded benzoic acid, and with chromic acid which produced benzaldehyde isolated as its semicarbazone.

Dehydration of $\alpha\gamma$ -Diphenylbutyl Alcohol with Sulphuric Acid

When $\alpha\gamma$ -diphenylbutyl alcohol is refluxed for three hours with 20% sulphuric acid, it produces 1,3-diphenyl-3-butene. After this has been allowed to stand, however, it does not deposit any crystals even when inoculated with a crystal of 1,3-diphenyl-1-butene. When this product is oxidized in acetone solution with potassium permanganate it yields β -phenylpropiophenone, m.p. 75° C. (oxime, m.p. 88° C.), and acetophenone, isolated as its semicarbazone (m.p. and mixed m.p. 207° C.), together with some benzoic acid mixed with another acid, probably phenylacetic acid. The production of acetophenone can be explained only by the presence in the mixture of 1,3-diphenyl-2-butene. Stoermer and Kootz (6) have shown that sulphuric acid brings about the isomerization of *cis*-1,3-diphenyl-1-butene to 1,3-diphenyl-2-butene. It is, therefore, likely in this case that some of the 1,3-diphenyl-3-butene isomerized to 1,3-diphenyl-1-butene, and that this was transformed by the sulphuric acid into 1,3-diphenyl-2-butene. During bromination, the last-named hydrocarbon lost hydrogen bromide, and the final product is an oil which could not be crystallized.

Pyrolysis of Heat-polymerized Styrene

Styrene was polymerized by heating in a sealed tube at 170° C. for 72 hr. The polymer was dissolved in benzene and fractionally precipitated with methanol. The fraction of average molecular weight 8000 (11 gm.) was pyrolyzed *in vacuo* according to the usual procedure (5), and the distyrene fraction, b.p. 144° to 150° at 3 mm., isolated by distillation (1.8 gm.).

This failed to crystallize even after inoculation with a sample of synthetic 1,3-diphenyl-1-butene. Half of this distyrene was dissolved in chloroform and brominated at room temperature as described above. The oily product was dissolved in methanol but failed to crystallize even in contact with a small crystal of the dibromide melting at 86.5° C. The oily bromide was then distilled. About one-third distilled at 170° C. at 1 mm. as a light-yellow oil, and a reddish-brown oil was left in the flask. This residual oil, dissolved in methanol, also failed to crystallize.

Pyrolytic distyrene, after standing several weeks, failed to develop the odor of benzaldehyde as 1,3-diphenyl-3-butene invariably does.

Preparation of $\alpha\gamma$ -Diphenylpropane

β -Phenylpropiophenone (10 gm.) was reduced by the method of Clemmensen and the oily product fractionated. A colorless oil, b.p. 120° to 122° at 1.5 mm., was collected. This fraction was dissolved in alcohol and treated with hydroxylamine hydrochloride and sodium acetate; the product dissolved in ether was extracted with several portions of aqueous sodium hydroxide. The oil recovered from the ether was redistilled, b.p. 124° C. at 2 mm. Wt., 4.6 gm. One gram of this $\alpha\gamma$ -diphenylpropane was nitrated according to the method of Bergmann and Fujise (1), and the tetranitro derivative recrystallized from chloroform-alcohol, m.p. 169° C.

Oxidation of $\alpha\gamma$ -Diphenylpropane

$\alpha\gamma$ -Diphenylpropane (1 gm.) was dissolved in glacial acetic acid and boiled for one-half hour with 0.4 gm. of chromic oxide, also dissolved in glacial acetic acid. This yielded 0.7 gm. of an oil which soon crystallized. Recrystallized from petroleum ether, it melted at 75° C. Admixed with an authentic specimen of β -phenylpropiophenone it did not depress the melting point. Half of the ketone was converted into the oxime, m.p. 87° C. before or after admixture with an authentic specimen.

Acknowledgment

The author wishes to take this opportunity to thank Dr. G. S. Whitby, Director of the Division of Chemistry, for his suggestions and continued interest.

References

1. BERGMANN, E. and FUJISE, S. Ann. 483 : 65-80. 1930.
2. FRIEDEL, C. and BALSCHN, M. Bull. soc. chim. 32 : 615-617. 1879.
3. KOHLER, E. P. and KIMBALL, R. H. J. Am. Chem. Soc. 55 : 4632-4639. 1933.
4. MIDGLEY, T., HENNE, A. L., and LEICESTER, H. M. J. Am. Chem. Soc. 58 : 1961-1963. 1936.
5. STAUDINGER, H. and STEINHOFFER, A. Ann. 517 : 35-53. 1935.
6. STOERMER, R. and KOOTZ, H. Ber. 61 : 2330-2336. 1928.

